

CHEMICAL ABSTRACTS

Vol. 17.

JANUARY 20, 1923

No. 2

1—APPARATUS

C. G. DERICK

A simple apparatus for electrometric titration. W. F. GARNER and C. A. WATERS. *J. Soc. Chem. Ind.* **41**, 337-8T(1922); 1 cut.—The electrode vessel consists of a tube with bulb at lower end, and two side arms sealed on immediately above the bulb, which are turned vertically downwards, tapering gradually to their open extremities. These not only serve in making connection with the soln. to be analyzed, but also aid in stirring when the entire vessel is rotated by means of a vertical shaft to which it is attached. Precaution is taken against loss of electrode soln. centrifugally during stirring and the formation of air-bubbles in the vessel itself. An outstanding advantage is that a volume of soln. as small as 5 cc. can be titrated. It has been satisfactorily used for detg. Ag with NaCl soln., Zn by ferrocyanide, and alk. sulfates by means of Ba salts, but is inapplicable to sulfates of metals giving insoluble hydroxides. T. F. BUEHRER

A new apparatus for exact gas analysis. K. A. SCHALLER and W. BERNDT. *Chem.-Ztg.* **46**, 972-3(1922).—The app. is extremely accurate, owing to the elimination of capillary errors and reducing the no. of cocks to a min. A poor cut and an incomplete description are given, with directions for operating. J. H. MOORE

A new instrument for sampling aerial dust. LEONARD GREENBURG and GEO. W. SMITH. *Bur. of Mines, Repts. of Investigations No. 2392*, 3 pp.(1922).—In this new impinger-bubbler type of app. the dust-laden air is caused by a blower to impinge at high velocity on a wetted glass surface, and subsequently to bubble through a liquid medium. The efficiency of the app. tested against tobacco smoke and silica dust, both gravimetrically and by means of the Tyndall effect, is from 9 to 31% higher than that of the sugar tube app. It possesses the additional advantage of low control errors, owing to simplicity of manipulation. T. F. BUEHRER

A tungsten furnace for experiments on dissociation and ionization. K. T. COMPTON. *J. Optical Soc. Am.* **6**, 910-12(1922); 1 cut.—A piece of sheet W, 0.002 in. thick or less, cut to right dimensions, is bent in the form of a cylindrical tube, and clamped at its ends between a steel "napkin ring" and a split rectangular steel block. The two blocks are mounted on water-cooled brass tubes, which serve as leads for the heating current and are insulated by means of short glass tubes. Loops of fine W-wire are drawn tightly around the furnace to prevent its bulging along the line of cut. The central electrode is a straight length of 20-mil tungsten wire, welded to heavier Mo leads. By adjusting the length of this wire, it is possible to secure equal potential drops along furnace and filament, so that they act essentially as equipotential electrodes. The filament is kept under sufficient tension to prevent sagging at the higher temps. The temps. were estimated from the resistance of the filament, after allowing for the resistance of the leads. To reach its m. p., the furnace requires 200 amps. at 6 volts, but a good white heat can be secured with 100 amps. The furnace is especially adapted to the investigation of radiating and ionizing potentials, of low voltage arcs in such gases as H₂, N₂, and I₂, and of the conditions of spectral excitation. In this manner the excitation of the first four and the convergence members of the Lyman series in atomic H have been studied at successively higher voltages. T. F. BUEHRER

New gasometer. ANON. *Chem.-Ztg.* 46, 974(1922).

J. H. MOORE

New steam valve. ANON. *Chem.-Ztg.* 46, 898-9(1922); 1 cut.—The valve is opened with a wheel, like a gate valve, but the movable part is a cylindrical plug and the seal is effected by means of special packing rings made of an elastic material instead of by the contact of 2 metal surfaces. Leakage is reduced, it lasts much longer than ordinary valves, and is easier to repair.

J. H. MOORE

Standardization of laboratory gas cocks. S. W. PARR. *J. Ind. Eng. Chem.* 14, 1105(1922); 3 cuts.—Various objectionable gas cocks now in general use are illustrated and discussed. A working sketch is given of a satisfactory cock to be used by the Univ. of Ill., which specifies optimum length of hose connection and size of corrugations. The outer edges of the corrugations have slight angles instead of round surfaces, permitting easy slipping on of connection tubing but resistance to its removal. T. F. B.

Description of a precision torsion spool instrument for thermoelectric measurements. GORGAS. *Z. Electrochem.* 28, 382-3(1922).—A new make of permanent magnet, moving spool type of thermoelec. instrument. Detailed description with figures.

P. D. V. MANNING

New vacuum drying plant. ANON. *Chem. Trade J.* 71, 451-2(1922).—A description of a new type of vacuum drier installed at the works of the Soc. matieres colorantes et prods. chim. St. Denis. It consists of an air-tight drying chamber contg. trays, a barometric condenser, a Delas steam jet air extractor for maintaining a vacuum in the condenser and drying chamber. This jet discharges into the steam space of the drier and thereby furnishes the heat for drying. The nozzle is simpler and requires less attention and repairs than a vacuum pump. In every case the actual economy is above 50%.

L. A. PRIDGEON

Acetylene generator. D. A. BROWN. Brit. 185,999, Dec. 7, 1921. In an C_2H_2 generator, H_2O is supplied continuously and the waste H_2O carrying the sludge in suspension escapes through an open-topped pipe sep'd. from the generating compartment by a foraminous partition provided at its lower end with a conical perforated screen. The carbide introduced through a shoot is caught on a dished tray.

Portable acetylene generator. O. R. GUNN. U. S. 1,433,003, Oct. 24.

Tank for storing gasoline or other dangerous liquids. P. F. A. RACINE. U. S. 1,432,619, Oct. 17. A tank designed for holding gasoline or similar liquids is submerged beneath H_2O in an outer tank and is provided with pipe connections for filling and discharge.

Compressed-vapor-heated evaporator. F. S. SANDBERG. U. S. 1,433,040, Oct. 24.

Distilling and evaporating apparatus. BLAIR, CAMPBELL & McLEAN, LTD., AND J. L. FERGUSON. Brit. 185,873, June 23, 1921. In app. for evapng. and distg. liquids in which the liquid passes upward through the tubes of a calandria to a vapor-separating chamber, a part of the concd. liquid flows from the chamber by a pipe to a tank and the other portion of the concd. liquid is returned by a pipe to the base of the calandria together with fresh liquid from a tank and pipe. Part of the vapor evolved in the chamber may be forced by an injector, fan, or pump, into the space surrounding the tubes of the calandria to serve as heating agent. The app. may be used under pressure or vacuum and as an element of a multiple-effect app. In a modified form of app., the end boxes of the calandria are divided by partitions to give the liquid a longer travel, and the fresh liquid is preheated by heat exchange with the concd. liquid and also with the condensate from the calandria, which may also be used to wash out the tubes of the calandria. The app. may be used for the recovery of benzene from oils and greases.

Jacketed evaporating vessel for treating milk or other liquids. C. R. MABEE. U. S. 1,433,141, Oct. 24.

Separators. T. H. MARYN. Brit. 186,016, April 28, 1922. App. for sepg. SnO_2 , or metal values such as Au, from wash dirt or sand by washing in H_2O , or other liquids such as hydrocarbon oils, comprizes an inclined sluice-box provided with moving knife-blades or share-hars to pass horizontally through the mass to split it up and loosen the pulp beneath the surface.

Apparatus for testing oils. F. H. M. KLEE. Brit. 185,814, June 3, 1921. App. for detg. the flash point or burning point of oils or other volatile liquids comprizes a vessel externally heated by elec. means, and adapted to contain, and allow ignition of, the liquid under test.

Apparatus for feeding finely divided shale, oil-sand or sulfur ore into retorts. J. T. FENTON. U. S. 1,432,170, Oct. 17. The air normally carried by the material is displaced by steam or other inert medium injected into a feed pipe with sufficient force to convey the solid particles through the feed pipe of a retort or still.

Apparatus for separating graphite from gang. S. J. SWANSON. U. S. 1,432,921, Oct. 24.

Apparatus for liquefaction of gases. P. R. McCRARY. U. S. 1,432,705, Oct. 17.

Gas-fired furnace for annealing or tempering. J. R. C. AUGUST. U. S. 1,432,946, Oct. 24. The furnace is adapted for hardening or tempering steel tools or for heating or annealing metals, glass or pottery.

Retorts. F. D. MARSHALL. Brit. 186,375, May 24, 1921. A rotary retort for drying, roasting, calcining, or distilling carbonaceous or other materials comprizes a shell having an inlet for heating gases, a spiral feeder for the material treated having a hollow interior serving as a gas outlet and an outlet for the residue.

Electron-discharge device. M. J. KELLY. U. S. 1,432,867, Oct. 24. Electrodes such as Ni or Mo are coated with oxide (by oxidation) or other black material and the coating is then removed from one of the surfaces of the electrode, to eliminate secondary and thermionic emission from grids.

Rotary filter. E. J. SWEETLAND. U. S. 1,432,134, Oct. 17. Mechanism is arranged for giving the filter a step by step movement within a tank.

Knife-edge bearings. S. C. BROWN and DENNISON & SON, LTD. Brit. 186,007, Feb. 18, 1922. The knife-edge centers, bearings, and end stops of weighing machines are electrically coated with a thin covering of Pb, Ni, Sn, Zn, Cu, etc., either separately or in combination, to prevent rusting, etc., from taking place. When the machines are in operation, the covering is cut through where the actual bearing contact takes place, so that there is steel-to-steel contact.

Oven thermometer. H. R. WHITTIER. U. S. 1,432,936, Oct. 24.

"Heat-storage" battery. G. L. HOGAN. U. S. 1,433,010, Oct. 24. Heat is liberated by crystn. of substances from supersatd. soln. in the device.

2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

The calculation of the molecular quadrupole moments from the equation of state. W. H. KESSOM. *Proc. Acad. Sci. Amsterdam* 24, 162-7(1922); *Verslag. Akad. Wetenschappen Amsterdam* 30, 199-205.—In the calcn. of the quadrupole moments from the experimentally detd. second virial coeffs., it is important to use the special reduced equation of state for the gas in question, not the mean equation of state, as used by Debye. Calcn. for H_2 gives the value of 1.10×10^{-25} (e.s.u. $\times \text{cm.}^2$) for the quadrupole moment.

GEORGE W. MOREY

Spontaneous incandescence of substances in atomic hydrogen gas. R. W. WOOD. *Proc. Roy. Soc. (London)* 102-A, 1-9(1922); cf. C. A. 16, 4136.—Incidental to very refined

spectroscopic measurements of H some interesting properties of at. H were discovered. Metals, oxides and other substances are raised to incandescence when introduced into a stream of at. H in a discharge tube. A W wire quickly comes to red heat and the secondary spectrum of H becomes strong in its vicinity, due to the *catalytic action* of the metal surface in causing recombination of the dissociation products of the discharge. The addition of O gas stops the heating of the wire by virtue of its power to "poison" the catalyst. At. H, practically free from mol. H₂, can be drawn by a pump from the central portion of a long vacuum tube excited by a high potential current. Fire-polished glass surfaces, such as the wall of a glass tube, have feeble catalyzing power, while fractured surfaces cause the rapid recombination of the atoms, and are strongly heated. An explanation of the necessity for the presence of H₂O vapor in H in order to produce the pure Balmer spectrum is therefore to be found in its action on the wall of the tube, which, when dry, catalyzes the at. H as fast as it is formed. W wires may be heated at a distance of 4 cm. from the discharge tube, and bits of Welsbach mantle are incandescent even at 20 cm. if the pressure is of the order 0.15 mm. At. H cannot travel past any point cooled by liquid air. Recombination of at. H takes place in about $\frac{1}{4}$ sec. The surprising ease with which practically pure at. H may be obtained filling the discharge tube not only during the flow of the current, but also during the intervals of low potential between the half-cycles of the alternating current when no current is flowing, suggest the possibility of numerous optical expts. G. L. CLARK

The condition of motion of the molecules in space. J. BOESEKEN, CHR. VAN LOON, DEX, AND HERMANS. *Proc. Acad. Sci. Amsterdam* 24, 198-204 (1922); *Verslag. Akad. Wetenschappen Amsterdam* 30, 216-22 (1921).—Theoretical. It is concluded that atoms which are not directly bound to each other exercise an action on each other in the molecule; that saturated non-cyclic molecules execute movements in which the parts of the molecule revolve in opposite direction or with different velocities around the single bonds as axes; and that in the saturated ring-shaped molecules with 6 and 7 carbon atoms the ring-forming atoms are not fixed in one plane, but they lie, free from tension, in a curved surface which travels through space in undulatory movements. G. W. M.

Experiments on structure with X-rays. FRITZ KIRCHNER. *Ann. Physik* 69, 59-80 (1922).—A *hot-cathode X-ray tube* especially designed for a. cs. without rectifiers is described in detail. The essential differences from the Coolidge type are the tube shape with side window and the U-shaped filament wire. By means of the *focussing method* of Seeman and Bohlin more accurate measurements and shorter time of exposure were enabled for the powder photographic method. The *lattice const. of Al* was detd. as a trial of the method from thin foil and controlled by the spectrum of NaCl. The value of d is 4.039 Å. *Electrolytically deposited layers* of different thicknesses of Cu, Pb and Fe were next subjected to analysis. In every case, even when very small c. ds. were used for the deposition, sharp interference lines were observed. A Pt mirror deposited on Cu on the other hand showed no interference lines. The *fibrous structure of rolled foils* was studied with Al foils. When the foil is oriented with the direction of rolling perpendicular to the cylinder axis of the camera, there is no reflection from the 022 planes, while this reflection appears very strongly when the direction of rolling is parallel to the axis. The structure is maintained by heating the foil to 270° though there are indications that the individual minute crystals have grown in size. The change in *structure of a 25% Ni-steel* in passing from a magnetized to non-magnetized state was next studied. The lines from the unmagnetized specimen indicate a face-centered lattice with $d = 3.580$. The picture of the magnetized alloy is exactly the same except that new lines appear at the right of the 111 line and between the 022 and 113 reflections. A new body-centered lattice with $d = 2.858$ is indicated. The difference of the lattice structures for the 2 states of Ni-steel lies in the fact that the no. of body-

centered unit crystals in the unmagnetized state must be very small. Upon magnetization this no. becomes very much larger, all the fundamental dimensions of both types of lattice in the alloy remaining unchanged. *Alloys of Cu and Au* all have face-centered lattices. An additivity law applies to the lattice consts.; for when these values are plotted against the mol.-% of one of the components they all lie on a straight line connecting the values of d for pure Au (4.067 Å.) and for pure Cu (3.615 Å.).

G. L. CLARK

The melting and freezing point of sodium chloride. J. B. FERGUSON. *J. Phys. Chem.* 26, 626–30 (1922).—The pure salt was melted in a Pt crucible under conditions to prevent reduction and the bare thermo-element which has been carefully calibrated as described by Adams (cf. *C. A.* 8, 1377) was allowed to freeze in place. The crucible and element were then heated in a silica test-tube in a resistance furnace. The f. p. taken as the highest temp. to which the salt heated up after the slight undercooling was $803^{\circ} \pm 1^{\circ}$.

H. M. McLAUGHLIN

Optical constants of sodium-potassium alloys. RAYMOND MORGAN. *J. Phys. Rev.* 20, 203–13 (1922).—The optical consts. of pure Na, of pure K, and of 7 Na-K alloys whose at. percentages of K were between 11 and 76 were detd. Mirrors were made by sucking the molten metal or alloy into evacuated glass cells, two of whose sides were plane. When the compn. of the alloy is about NaK the refractivity is at a max. value, 0.137; and the absorptive index is at a min. value, 12.5. A change in temp. seemed to cause a change in optical consts. for some of the alloys, but for other alloys no such change was evident. A table of values is given.

F. E. BROWN

Measurement of mercury vapor pressure by means of the Knudsen pressure gage. CHARLES F. HILL. *Phys. Rev.* 20, 259–66 (1922); cf. *C. A.* 16, 3573.—Two series of detns. were made, comprizing observations at 19 different temps. between -0.7° and 34.9° . The value at -0.7° is 0.00033 mm. of Hg; at 34.9° , it is 0.00575 mm. The readings lie on a smooth curve which is believed to give the vapor pressures of Hg between these temps. correct to within 3%.

F. E. BROWN

The vapor pressure of ternary mixtures. A. W. PORTER. *Trans. Faraday Soc.* 18, 19–21 (1922).—In an earlier paper (*C. A.* 15, 3785) it was shown that the Duhem-Margules equation can be extended to systems of higher order than the binary. The data of Resanoff, Schulze, and Dunphy (*C. A.* 9, 402) for the ternary system toluene- CCl_4 -ethylene bromide are shown to agree well with the figures calcd. from these equations.

JAMES M. BELL

Study of catalytic actions at solid surfaces. VIII. The action of sodium carbonate in promoting the hydrogenation of phenol. E. F. ARMSTRONG AND T. P. HILDTCH. *Proc. Roy. Soc. (London)* 102A, 21–7 (1922); cf. *C. A.* 16, 1348.—Hydrogenation of liquid phenol in the presence of Ni proceeds to completion readily at 150 – 190° with the production of cyclohexanol and cyclohexanone in the proportion of about 95 to 5. The rate of the reaction is notably accelerated by the presence of small quantities of mildly alk. salts, the most suitable being anhyd. Na_2CO_3 . When 100 g. phenol were subjected for 1 hr. at 180° to a pressure of 80 lb./sq. in. of H_2 , the max. yields were obtained when Na_2CO_3 was present the amt. of about 25% of the wt. of Ni. Further, in the absence of Na_2CO_3 , the rate of hydrogenation follows the unimol. equation with respect to the phenol, while in the presence of Na_2CO_3 the action is more nearly represented by a linear relation. This result suggests that the action of the carbonate is a protective one with respect to the catalyst, rendering the latter free to exercise its normal function. **IX. The action of copper in promoting the activity of nickel catalyst.** E. F. ARMSTRONG AND T. P. HILDTCH. *Ibid.* 27–32.—The higher activity of mixed Cu-Ni catalysts over Ni itself in hydrogenation is found to be due to conditions of surface area. Comparison between the effect of Ni distributed to display its max. effi-

ciency and the effect of mixed Cu-Ni similarly mounted shows no advantage of the latter. Prepn. of a Cu-Ni catalyst is possible at 170-180°, whereas Ni compds. alone are not reduced by H below 300°. The Ni and Cu must not simply be intimately mixed by being precipitated together, but must also be contained in the same complex carbonate mol. prior to reduction by H. It is suggested that in the reduction of the complex compd., heat from the reduction of the Cu is sufficient to raise the temp. locally to the temp. required for the reduction of Ni. These results have been obtained by following the hydrogenation of cottonseed oil.

JAMES M. BELL

Catalytic hydrogenation and the potential of the hydrogen electrode. JAMES B. CONANT AND HAROLD B. CUTTER. *J. Am. Chem. Soc.* **44**, 2651-4(1922).— $\text{Me}_3\text{C}:\text{CHCO}_2\text{H}$ in 0.1 N HCl is reduced by H, H_2PtCl_6 , gum arabic and "seed" colloidal Pt to $\text{Me}_3\text{CHCH}_2\text{CO}_2\text{H}$ but is not affected by CrCl_3 even after standing for several months. The potential of the H in the 1st case is about -0.05 volt on the normal H electrode scale, and that of a mixt. amts. of Cr'' and Cr' ions is -0.40 volt, i. e., the reducing agent in this case is about 0.3 volt more powerful than the H-catalyst combination and yet does not accomplish the reduction. The conception of reduction potential as applied to irreversible catalytic hydrogenation does not seem to be of value in correlating known facts. On the other hand, although the very fact that a certain process of reduction or hydrogenation is irreversible prevents the application to it of the usual thermodynamical equations and it is impossible at present to measure or define its oxidation-reduction potential, yet it is known, in a rather qual. way, that in many instances the possibility of bringing about a certain irreversible reduction depends on the oxidation-reduction potential of the reagent employed. Thus, maleic acid is reduced to succinic acid by CrCl_3 but not by $\text{Na}_2\text{S}_2\text{O}_4$ or TiCl_3 while $(:\text{CHBz})_2$ is reduced to $\text{CH}_2(\text{Bz})_2$ by all of these reagents, and it can be confidently predicted that a stronger reducing agent of nearly the same oxidation-reduction potential as $\text{Na}_2\text{S}_2\text{O}_4$ will reduce the diketone but not the acid whereas a reducing substance with as low a potential as CrCl_3 will reduce both substances. In the light of the above results, it is perhaps reasonable to suppose that the reduction of maleic acid and $(:\text{CHBz})_2$ and the catalytic hydrogenation of $\text{Me}_3\text{C}:\text{CHCO}_2\text{H}$ represent different types of processes. It is suggested that the first involves the addn. of electrons and H ions ($\text{B} + 2\text{e}^- + 2\text{H}^+ \longrightarrow \text{BH}_2$) and the second the addn. of H atoms only ($\text{B} + 2\text{H} \longrightarrow \text{BH}_2$). The first equation represents a case of electronic reduction of the inorg. type which is peculiar because it is irreversible and because it involves addn. of H ions as well as of electrons. C. A. R.

Growth and dissolving of crystals. G. MASING. *Naturwissenschaften* **10**, 899-908 (1922).—A review and general discussion, particularly of the work of R. Gross.

C. C. DAVIS

The production and measurement of high vacua. F. H. NEWMAN. *Beams* **11**, 717-22(1922).—A review profusely illustrated.

D. MACRAE

Color designation. HEINRICH TRILLICH. *Farben-Ztg.* **27**, 3323-4, 3379-80 (1922).—Cf. C. A. **16**, 2065, 3238.

F. A. WERTZ

Carbon dioxide and sulfur dioxide content of Berlin air. OTTO HAEHNEL. *Z. angew. Chem.* **35**, 618-20(1922).—Weathering of stone and metal structures has been observed to take place more rapidly in cities and industrial centers than in the country. This difference appears to be due to the higher concns. of acidic gases in the air. Analysis of air in Berlin showed 0.003281 g. of SO_2 and 0.4048 g. of CO_2 per 100 l. Weathering due to these gases in the air is greater on foggy or damp days than on rainy days, owing to the higher concns. produced with smaller quantities of H_2O . T. S. CARSWELL

Properties of dibenzoylcystine (WOLF AND RIDDAL) **11A**. Control of gaseous conduction (STEINMEYER, et al.) **4**. Dielectric strength of the vacuum (HAYDEN) **4**.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Bombardment of metal surfaces by slow-moving electrons. H. E. FARNSWORTH. *Phys. Rev.* 20, 358-74(1922).—See C. A. 16, 3585. MARIE FARNSWORTH

Dissociation of carbon in the intensive arc. LOUIS BELL AND P. R. BASSETT. *Science* 56, 512(1922).—During expts. with the extremely powerful arcs used in the Sperry search-lights a peculiar spectrum was noted in the "negative tongue" which appears at currents of 100 amps. or more. An image of this flame was examd. with a direct vision spectroscope and some 15 well defined lines were found. Of these, 7 were good coincidences with the most conspicuous of the He lines, and 2 others with H_{α} and H_{β} . All indications point to the dissoc. of a certain proportion of C nuclei with the consequent appearance of He. The H lines may be due to water-vapor absorbed by the soft C core, or perhaps to further dissoc. W. F. MCGREGGERS

The stability of radium solutions. AUG. BECKER. *Z. anorg. allgem. Chem.* 124, 143-52(1922).—Standard $RaCl_2$ solns., contg. from 0.02115 to 0.00001897 mg. Ra/g., some HCl and a little $BaCl_2$, which had been used in the analysis of pitchblende in 1914, were once more compared with the same pitchblende in 1922. The Ra content was found unchanged, on the assumption of const. Ra content of the ore, within the working error (1%). NORRIS F. HALL

The photoelectric theory of flame conduction. ERICK MARK. *Ann. Physik* 65, 657-74(1921).—In a previous communication (C. A. 11, 1080) M. has endeavored to explain the ionization in flames as due chiefly to the liberating of electrons from the metal ions of the alkali flames, using the photoelec. hypothesis, in place of Lenard's theory. For Elster and Geitel have shown that the elementary alkali metals give off electrons with great readiness, under the influence of red and even of infra-red light, as well as of ultra-violet light. It may, therefore, be assumed that positively charged alk. atoms constitute the normal condition in a flame, and that the absence of an observed photoelec. effect with external illumination, is due to the fact that the ionic density in the flame has already reached a satn. value. The present paper contains a crit. discussion of the various terms in the previously deduced equations, and of related exptl. facts and theories. No new exptl. evidence is presented. R. T. BIRGE

The ionization in a Geissler tube discharge. ERICK RUMPF. *Ann. Physik* 66, 50-70(1921).—A continuation of previous work (cf. C. A. 12, 1852; 14, 1259). The rate of disappearance of ionization in a Geissler tube, after opening the circuit, depends both upon the rate of recombination of the ions, and upon the rate of diffusion. At low pressures, where little previous work has been done, the latter factor may become very important. The diffusion is smallest, relative to the rate of recombination, where the ionic density is greatest and also where it is most uniform. Both conditions are best satisfied where the negative glow passes over into the Faraday dark space. With a slight modification of R.'s previous exptl. arrangement, it was found that at the point mentioned the measured rate of recombination was practically unaffected by the diffusion. This rate depended greatly upon the condition of the electrodes, as well as upon the dimensions of the tube. By using very clean electrodes, at a sufficient distance apart, the recombination const. in air at 0.2 mm. of Hg pressure was found to be 3.5×10^{-14} . R. T. BIRGE

The thermionic work function of tungsten. C. DAVISSON AND L. H. GERMER. *Phys. Rev.* 20, 300-30(1922).—Measurements have been made simultaneously by two methods for the same segment of a uniformly heated filament. The filament, of 0.0755 mm. diam. and with 3 finer W leads welded to it 3.85 cm. apart, was kept stretched, by means of a Mo spring, between two Mo plates used to apply an elec. field and to re-

ceive the space current, the ends of the filament being surrounded by guard boxes to limit the emission to the section of the filament between the potential leads. All parts were sealed inside a tube and so thoroughly out-gassed by alternately baking the tube and heating the metal parts that the residual pressure during the measurements was only about 10^{-7} mm., as measured with an ionization manometer. (1) In the calorimetric method, the equiv. voltage of the work function was computed from the relation $\phi = 2EI(\Delta E/i)/[E - I(dE/dI)]$, where E is the voltage across the segment and I the current through it, and ΔE is the voltage change when the space current i flows from the filament, I being kept const. Observations from 2070° K. to 2300° K. show an apparent increase for ϕ of about 2% in this range, considerably greater than is to be expected theoretically. At 2270° K., when correction is made for the asymmetry of the elec. shielding (-2.24%) and for the radiation from the plates heated by the space current ($+4.12\%$), ϕ comes out 4.91 ± 0.05 v. (2) In the temp. variation method, assuming Richardson's equation $\log i = \text{const.} + \frac{1}{2} \log T - (\phi/kT)$, measurements of the emission in the range 1930° K. to 2300° K. give for ϕ a value 2.7% less than the value obtained calorimetrically, a difference believed to be greater than the probable error of the measurements. It is suggested that the theory of conduction of electricity in metals be modified thus—the thermal energy of conduction electrons is supposed to be $\frac{1}{2}kT$ by the classical theory upon which the above computations of ϕ are based. If, however, the energy is taken to be practically zero then the same data lead to 4.52 and 4.48 v. for the values of ϕ by the two methods and the agreement is within the probable error of the measurements.

MARIE FARNSWORTH

Theory of ionization by cumulative action and the low voltage arc. K. T. COMPTON. *Phys. Rev.* **20**, 284-99(1922); cf. C. A. **16**, 2070.—Equations for the case of coaxial cylindrical electrodes are derived for the proportion of mols. partially ionized (1) by direct impact and (2) by resonance. The substitution of experimentally detd. values leads to the conclusion that, under normal circumstances, partial ionization by photo-impact is many times as great as that by electronic impact alone and is necessary and sufficient to account for the observed ionization. The possibility is also discussed of complete ionization by successive photo-impacts. The theory of the low-voltage arc is developed. Expts. with the low-voltage arc in Hg vapor indicate that the striking voltage is about 5.6 instead of 4.9 v., and that the arc may be dependent on either the 4.9 v. (2536 Å) or the 6.7 v. (1849 Å) radiation according to the age of the vapor. Thus there seems to be two metastable states of the neutral Hg atom. It is pointed out that resonance radiation must also be the chief factor in temp. ionization both in the elec. furnace and in the sun and other stars.

MARIE FARNSWORTH

The excitation and ionization potentials of neon and argon. G. HERTZ. *Proc. Acad. Sci. Amsterdam* **25**, 179-87(1922).—A new method has been devised for the accurate relative measurement of radiation potentials, based on the detection of the voltage or voltages where electrons with zero velocity alone appear. With the type of app. used, a sharp peak appears at such points, on the current-voltage curves, instead of the more or less indefinite break of the ordinary method. A slight modification of the new method also enables the relative ionization potential to be obtained. Basing all results on Franck and Knipping's value of 20.45 v. for the first radiation potential of He, H. obtains for Ne radiation potentials of 17.35 and 19.15 v., and an ionization potential of 22.2 v. A gave two strong radiation potentials of 12.25 and 13.7 v., and a less distinct one at 14.7 v.—also an ionization potential of 16.0 v. Current-voltage curves for all these data are given. The results for Ne fit quant. into Paschen's series-analysis of the Ne spectrum (*Ann. Physik* **60**, 405(1919)) and indicate in addn. the stable energy state of Ne as $0.55 = 179,800 \pm 1000$ (frequency units). The results agree also with Horton and Davies' observations on the voltages at which Ne series were excited

(*C. A.* 15, 2781) but do not agree with their radiation and ionization potential results (11.8, 16.7, and 20 v.). The new results for A indicate a series scheme having for the stable state $0.5s = 130,000 \pm 1000$, while $1.5s = 30,400$, and $2p = 18,600$ (approx.). They do not agree with Nissen's spectral scheme (*C. A.* 14, 3366) to which however other objections may be raised.

R. T. BIRGE

The spectral system of Röntgen rays. L. DE BROGLIE AND A. DAUVILLIER. *Compt. rend.* 175, 685-8(1922).—The work of Bohr, Sommerfeld, Wentzel, and others has indicated the theoretical assignment of 3 quantum numbers to each energy level of X-ray spectra. The authors present, for the first time, a table giving the complete scheme of X-ray lines, on this theory. [However, the number of levels and the scheme of assigned quantum numbers disagree in general with Bohr's 1921 theory of at. structure.—ABSTRACTOR.] The table indicates the terminal levels for each line, including 103 lines allowed by the selective principle but not yet observed, and 8 faint L lines observed but not allowed by the principle. The observed lines as listed comprise 5 K, 34 L, 6 M, and 8 N lines. No O or P series lines have been found as yet. The latter should fall in the visible spectrum.

R. T. BIRGE

The intensity of reflection of Röntgen rays of various wave lengths. ERNST WAGNER AND H. KULENKAMPF. *Ann. Physik* 68, 369-413(1922).—This investigation was prompted by the desire to obtain the true energy distribution in continuous X-ray spectra. The chief unknown factor hitherto has been the dependence on wave length of the reflecting power of the crystal. Monochromatic radiation was obtained by reflection from a crystal K' . The reflected beam was then reflected from a second crystal K'' , placed close to K' , the two reflecting surfaces being parallel. K'' was steadily rotated through a small angle (about $8'$ of arc) and the "rocking curve" (ionization plotted against angle) was thus obtained. The area under this curve when compared with the directly transmitted energy (i. e., with K'' removed) leads to a usable "absolute" value of the reflection coeff. (R), as has been shown by Bragg and co-workers (*C. A.* 15, 1453). (1) By using essentially the exptl. arrangements already described by Wagner (*C. A.* 13, 3072) the value of R was obtained for the (100) planes of calcite and rock salt, for wave lengths of 1.39 to 1.93 Å. (2) The R for calcite was found to be nearly independent of λ , while for rock salt it decreased greatly, with increasing λ . On the av. rock salt reflects 3 times as strongly as calcite. But with a stationary crystal and monochromatic radiation, calcite can show a stronger reflection, owing to the smaller angular area ("rocking" angle) over which the energy is distributed. This angular area depends on the character of the crystal surface. (3) The abs. values of R for the 2 crystals were checked by comparative measurements, a single reflection being used. (4) The relative reflecting power in the first and second order (100) in each crystal, for the wave lengths of the Cu and Fe $K\alpha$ line, was measured and found to depend upon the wave length in a manner to be expected theoretically. (5) Values of R for short wave lengths as detd. by Bragg (for rock salt) and by Davis and Stempel (for calcite) were included in a comparison of the dependence of R on λ . The calcite values were found in good agreement with theory, those for rock salt in passable agreement. (6) The values of R obtained in this investigation were used to correct the measured energy distribution curves of the continuous spectrum from a Ag anticathode, with a voltage of 10,500. The two corrected curves were identical, thus confirming the above work. In making the correction it is necessary to consider important differences between the reflection of monochromatic and of continuous radiation. A further correction for the absorption of the radiation in all media through which it passes then leads to the true intensity distribution in the continuous X-ray spectrum of Ag, from about 1.2 to 2.2 Å.

R. T. BIRGE

Visible and infra-red radiation of hydrogen. F. S. BRACKETT. *Astrophys. J.* 56,

154-61(1922).—Radiation from the central section of a long discharge tube was analyzed by means of a rock salt prism spectrometer having mirrors for both collimator and telescope. The energy was measured by a sensitive thermo-junction. Two known and 3 new members of the Paschen series were observed at wave lengths given by the formula $\nu = N(1/3^2 - 1/m^2)$, where $m = 4$ to 8. The first 2 members of a new series were found at 4.05 and 2.63 μ , fitting the formula $\nu = N(1/4^2 - 1/m^2)$, where $m = 5, 6$. On the Bohr theory these series are due to electrons falling from outer orbits to the third and fourth orbits, resp. Some unidentified lines are shown in a figure giving the energy distribution between 0.6 and 4.8 μ . The first Paschen line was found to increase in intensity more rapidly than H α with increase of current. K. BURNS

Revision of the series in the spectrum of strontium. F. A. SAUNDERS. *Astrophys. J.* 56, 73-83(1922).—The structure of the systems of triplets and singlets, belonging to the neutral atom of Sr, is remarkably similar to that of the corresponding series of Ca. Measurements by Randall, King, and S. were used. The sources were: sparks, arcs in air and *in vacuo*, tube-resistance furnace, and red-hot quartz discharge tube. The spectrum is covered from 0.22 to 3.06 μ . The wave lengths of many lines are re-vised and 70 new lines are recorded. The values of the limits of all the series have been improved, and the various terms have been computed. Tabular details are given for 4 types of triplets, 4 of singlets, 4 combination series in the former system and 3 in the latter, and 5 inter-system combination series. Some of these 20 series are very faint, represented by only one term; about half are new. New types of singlet series were found, corresponding to formulas (1P)-(mX), (1p)-(mX), (1P)-(mY), etc. The terms are all so large that these series cannot be of the sort suggested by Sommerfeld. Three singlet lines are found in the spectrum of Ca which point to Ca series similar to those last mentioned for Sr. K. BURNS

The spectrum of neutral helium. LUDWIG SILBERSTEIN. *Astrophys. J.* 56, 119-31(1922).—Since the neutral atom of He has 2 electrons, the theoretical treatment of the spectral lines involves the problem of 3 bodies. The general soln. of this problem cannot be effected. S. has tried the particular soln. resulting from permanent collinearity, but the formula so derived fits none of the He lines. By assuming that the mutual perturbation of the electrons is negligible the following formula was derived: $\nu = 4N(1/n_1^2 - 1/m_1^2 + 1/n_2^2 - 1/m_2^2)$. By choosing the proper integral values, up to 9 for n and up to 32 for m , the formula gives 84 of the 111 known lines, usually within a fraction of an Ångström. The resulting classification does not correspond to the customary series arrangement. Yet the success of the formula suggests that the force between intra-atomic electrons may be much less than that given by the Coulomb law. K. BURNS

Practical spectrographic analysis. W. F. MEGGERS, C. C. KIESS AND F. J. STIMSON. *Bur. Standards, Sci. Papers* 18, 235-55(1922).—A brief review of various methods which have been proposed for chem. analyses by means of the spectrum is followed by a detailed description of the principle, app., and procedure employed in making quant. analyses from the spectra of condensed sparks. The method is based on the well known fact that with the diminution of an element in a mixt., its spectrum becomes simplified, more and more lines disappearing, until only a few of the most sensitive lines remain when a minute trace of the element is present. After correlating the partial spectra of elements in a graded series of alloys with the known chem. compn., similar unknown samples may be analyzed by comparison with these standards. It is emphasized that the interpretation of quant. results must be based upon standardized app. and the observation of conditions. The practical possibilities in spectral methods are recommended as an aid to wet chem. analysis, especially where the chem. methods are inapplicable to small samples, insensitive to very small amts. and in cases of tedious rou-

tine. Such applications are illustrated by 3 examples dealing with the quant. detn. of impurities in various samples of Sn, Au and Pt. Other applications to problems in chemistry, metallurgy, mineralogy, physics, biology, etc., are suggested. W. F. M.

Experiments on structure with X-rays (KIRCHNER) 2.

4—ELECTROCHEMISTRY

COLIN G. FINK

New type of French electric furnace. R. SYLVANY. *Iron Age* 110, 763-4(1922).—A new type of elec. furnace developed by T. Levoz was used in France during the war for the production of high speed steels. This furnace is a closed crucible with a single opening for charging, making addns., and pouring. The current enters through a large vertical C electrode in the roof. The horizontal section of this electrode is $\frac{1}{2}$ that of the furnace crucible. With d. c. this positive electrode is hollowed out and forms a heat reflector. The bottom electrodes are bundles of Fe wires embedded in the hearth and in the lateral linings of the furnace. The lateral lining presents a larger surface than the bottom of the furnace and permits the no. of embedded Fe wires to be increased and their cross section decreased. Wires of 6 to 10 mm. in diam. are used. The small section metal conductors produce a more uniform distribution of elec. current and more uniform heating of slag. The lateral electrodes are arranged in two superimposed rows, the lower electrodes for fusion, the upper for refining. Current can be switched from fusion to refining electrodes or taken from both rows at once. L. J.

The manufacture of electric furnace steels. JOHAN LEFFLER and ASSAR GROENWALL. *Rev. metal.* 19, Abs. sec., 413-7(1922).—A brief resumé of the Swedish practice. With the introduction of the elec. furnace in 1910-11, the tonnage has been increased from 132 to 75,684 in ten years. The Groenwall Triphase is a popular design and is used extensively. Analyses of charcoal, furnace gases, slags, Lancashire and Bessemer ores and their products are given. Electrodes are 60-70 cm. in diam. and 2-3 m. long; their consumption varies from 15 to 5 kg./ton of metal, according to quality. The power consumption varies from 2000 to 2700 kw.-hr./ton, the efficiency varying from 83 to 92% and increasing with the number of furnaces operating. W. A. MUDGE

Melts gray iron electrically. W. E. CAHILL. *Foundry* 50, 420-1(1922).—An all-scrap charge was melted and refined on a basic hearth under a reducing slag, in an 800-kw., 3-phase, 2-ton Heroult furnace. Si, Mn, and any other desired addns. are obtained from ferro-alloys. On intermittent operation, single voltage, 893 kw.-hrs. are required per ton of steel, and 784 kw.-hrs. per ton of iron. With dual voltage these figures are reduced to 851 and 709, resp. A high quality gray iron of very fine grain is obtained. S varies between 0.03 and 0.06, and P between 0.2 and 0.5%. Very little hearth repair is required; usually 10-20 lbs. of magnesite will suffice. W. F. R.

Heating steel in the electric furnace. M. SILLON and V. GUILLERMIN. *Rev. ind. minerale* 1, 249-57, 590-2(1921).—A study of the heating effect of the current in one, two and three phase arc furnaces, having different electrode arrangements.

W. E. RUDER

Resistance type electric furnace tested for steel melting. ANON. *Chem. Met. Eng.* 25, 667(1921).—See C. A. 15, 3791.

LOUIS JORDAN

A simple electric crucible furnace for melting aluminium. A. G. LOBLEY. *Trans. Am. Electrochem. Soc.* 42, preprint(1922).—Nichrome ribbon resistor wound in helix is set on shelves around a crucible, which has capacity of 35-40 lbs. of Al. It carries a current of 112 to 200 v. and 11.4 to 20 amp. Outside dimensions of the furnace are 32 in. \times 33 in. Cost figures show this furnace more economical than the gas furnace, metal losses

being less and a cleaner product being obtained. A diagram showing simple construction is given.

A. H. DICK

The Greenawalt electrolytic copper extraction process. WM. E. GREENAWALT. *Eng. Mining J.-Press* 114, 712-7(1922).—A description of G.'s process as applied to Cu leaching and electrolytic deposition. The deleterious effect of ferric salts in Cu solns. is avoided by a more rapid reduction by SO_2 . Reduction by the ordinary tower method as now employed is slow; this is speeded up by the use of special reducer units which, as shown in the cuts, are quite similar to the so-called dasher-washers as used in the Mond gas practice. Two methods are used: (1) SO_2 , (2) CuS, and a combination of the two. The general arrangement of a G. plant comprises a series of SO_2 reducers and Cu deposition cells and a flow of liquor so that there is a regulated stream of reduced soln. from reducers to cells and of electrolyzed soln. to reducers in a sort of closed circuit, while at the same time there is an advance flow through the whole series. Depleted soln. is then returned to the ore leaching and further treatment. It is found practical to deposit 1.4 lb. Cu per kw.-hr. with Pb anode, which is claimed to be 50% better efficiency than ordinarily realized. The significant fact is that it is practical to treat concentrates or high grade Cu ores. Description and cuts of a general arrangement are shown. When the $\text{Fe}_2(\text{SO}_4)_3$ content of soln. is high it is reduced by use of CuS and a discussion of the practical application of the process is given, showing wherein it is of material advantage over present methods.

L. D. VORSE

The electrolytic recovery of zinc. SAMUEL FIELD. *Trans. Faraday Soc.* 17, 400-41(1922); cf. C. A. 15, 25; 16, 3264.—A more complete paper including costs in English practice.

P. D. V. MANNING

Electrolytic recovery of zinc. W. PALMAER. *Tekn. Tids. Uppl. A.* 52, 610-4, 657-60, 705-10(1922).—An address.

A. R. ROSE

Applications of electric equipment in the metallurgy of nickel. J. L. McK. YARLEY. *Eng. Mining J.-Press* 114, 810-12(1922).—Ni has been recovered mainly by the typical pyrometallurgical method. Y. gives a Canadian electro-method for obtaining Ni as the by-product of Co-Ag ore refining. The article deals chiefly with a leaching-electrolytic method for getting Ni from bessemerized mat. H_2SO_4 leaching dissolves a large quantity of Cu and but little Ni from the mat. The residue is cast into anodes and refined Ni is produced by electrolytic deposition. The H_2SO_4 liquor is electrolyzed for Cu, using insol. anodes. Flow sheet and details of construction are given.

A. H. DICK

The application of contractometer to the study of nickel deposition. E. A. VUILLEUMIER. *Trans. Am. Electrochem. Soc.* 42, preprint(1922); 1 illus. —Ni deposited on thin sheets of Pt causes the cathode to bend toward the anode. The bending is accurately measured by means of a contractometer which is described and its accuracy shown. Slowing up of the pointer is paralleled by a change in the structure of the deposit. Delays and spurts in the contraction arise when little or no H is liberated during the deposition. The structure of the deposit is influenced by the metal-ion concn., H-ion concn., current density, temp., etc. In general, a soln. giving large contractometer readings gives deposits showing marked tendency to peel (excess H in deposit).

W. H. BOYNTON

Progress in the use of storage batteries. H. BECKMAN. *Z. Ver. deut. Ing.* 66, 77-83, 109-11(1922).—A survey of the present large use of storage batteries and the outlook for future growth. The newest types of battery-driven suburban trains, mine and switching locomotives, and elec. mules, and batteries for submarine, automobile, and truck use, are described with drawings and photographs. High gasoline costs and cheap hydroelec. power make the more extensive use of storage batteries most desirable.

W. E. RUDER

High-voltage storage battery for use with electron tube generators of radio-frequency currents. E. L. HALL, AND J. L. PRESTON. *J. Optical Soc. Am.* 6, 177-82(1922).—The app. consists of wooden trays set one upon the other. Each tray contains 48 cells set in paraffin and gives 100 v. Paraffin covers are used. By use of several trays currents up to 600 v. have been produced. Good for small const. current. The life of the batteries is at least four years. Diagrams are shown.

A. H. DICK

Separation of dust from gases by electricity. JOH. KÖRTING. *Z. Ver. deut. Ing.* 66, 719-22(1922).—A review of the use of the *Coltrel process* in Germany and other countries.

D. MACRAE

Control of gaseous conduction. C. P. STEINMETZ, J. B. WHITEHEAD, J. E. SHRADER AND V. BUSH. *J. Am. Inst. Elec. Eng.* 41, 889(1922).—Discussion of paper by Bush and Smith (*C. A.* 17, 27).

D. MACRAE

The multiversal test set. ANON. *Beama* 11, 753-5(1922).—A new sensitive Wheatstone bridge outfit for testing insulation resistances, cond. of wires, etc. Voltages range from 0.75 milliv. to 1,200 v. Details are included.

C. G. F.

Dielectric strength of the vacuum. J. L. R. HAYDEN. *J. Am. Inst. Elec. Eng.* 41, 852-4(1922).—The dielec. strength of the perfect vacuum would be the voltage gradient which, by its electrostatic stress, expels from the electrodes ions alone or ions and metal vapors. The breakdown voltage was detd. between 2 spheres, 1 cm. diam., of pure Mo 0.306 cm. apart in a very thoroughly exhausted 20 cm. kenotron bulb. It was concluded that the dielec. strength of the perfect vacuum is not less than 1235 kilovolts per cm. This is 25 times the dielec. strength of air in the same gap between the same two spheres.

D. MACRAE

Repulsion effect upon the poles of the electric arc. A. SELLERIO. *Phil. Mag.* 44, 765-77(1922).—After applying some corrections (indicated by Duffield) to his earlier measurements (*Nuovo cimento* 11, 67(1916)) S. compares his results with those of Duffield, Buruham and Davis (*C. A.* 14, 3358) and finds them in good general agreement. The total repulsion, P , between the two poles of the arc increases with the current. The range of P is less than 10 dynes for currents up to 20 amps. P varies little with the arc length, except when it approaches 0, when P becomes greater. The carbon quality has a great influence on P . It appears that metallic salts increase the pressure on the cathode and diminish it on the anode. With uncured carbons the repulsion on the cathode appears smaller than that on the anode, but the sp. pressure, f , per unit of crater surface is greater on the cathode. The range of $p+$ and $p-$ is about 10 dynes/sq. cm. It is not yet certain whether the law connecting P with current is linear or whether a current min. is required. P calcd. by Duffield from the recoil hypothesis, by taking for the velocity of the C particles their at. speed, is too great. S. shows that the propulsion velocity of C from the $+$ crater is in better agreement with expt.

S. C. LAND

The valve action of certain minerals used as electrodes in lighting arcs. STANISLAW BOROWIK. *Z. Physik* 11, 55(1922).—Certain minerals, such as $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ or FeS_2 , allow current to pass only when serving as anodes in lighting arcs. This valve action ceases abruptly when the electrodes are less than 0.5 mm. apart. Currents at least as high as 30 amp. can be carried, although the best action is obtained if the frequency is not too low. The secondary current from an induction coil is readily rectified.

F. O. A.

Method of testing plates from piezo-electric crystals. W. G. Cady. *J. Optical Soc. Am.* 6, 183-5(1922).—The article describes convenient and sensitive app. for testing and comparing plates cut from piezo-elec. crystals. Plates tested are subjected to light periodic stresses of audible frequency by means of a huzzer, and the quality of the plate is judged by the response in a telephone receiver. Plates

may be tested for longitudinal and transverse effects. The app. permits exploring a plate of any size and serves for detecting changes in polarity or marked variations in piezoelec. const. Results are roughly quant.

A. H. DICKE

Treating copper-nickel solutions (Brit. pat. 185,859) 9.

Storage battery. W. H. WOOD. U. S. 1,432,937, Oct. 24. Pb oxide paste is mixed with finely divided cellulosic material such as nonresinous wood or cotton which is afterward removed by the action of H_2SO_4 in order to increase the porosity and reactivity of the material.

Storage battery. H. L. EDNEY. U. S. 1,432,845, Oct. 24. Grids for positive storage battery plates are filled with a paste comprizing PbO_2 , dil. H_2SO_4 , collodion, $Al_2(SO_4)_3$, glycerol and $NaHCO_3$ or other ingredients to produce a gas and the filled plate is dried and formed.

Storage battery separators. W. H. WOOD. U. S. 1,432,939, Oct. 24. Strands of hair from which the scaly exterior portions have been removed by Na_2SO_3 or $Ca(OH)_2$ are embedded in separators of rubber compn. to give porosity.

Storage battery separators. W. H. WOOD and H. E. SMITH. U. S. 1,432,938, Oct. 24. Threads of cotton and wool or other mixed fibers (one only of which is sol. in H_2SO_4) extend through separators or rubber compn. or other insol. material.

Paste for storage battery plates. T. A. WILLARD. U. S. 1,432,508, Oct. 17. A paste for negative storage battery plates is formed of Pb oxide together with 0.6% of wood dust which serves to improve the porosity of the active material.

Electric supply systems. T. F. WALL. Brit. 186,467, July 19, 1921. The power factor of an a. c. supply system is improved by introducing a capacity effect in the form of a cell comprizing a pair of similar accumulator electrodes. The accumulator or cell may be placed in the exciting circuit of an induction generator or in the rotor circuit of an induction motor. The electrodes may be spongy lead plates or "pasted" plates and the electrolyte may be dil. H_2SO_4 .

Desulfating accumulator electrodes. W. O. CARBUTT. Brit. 185,797, May 11, 1921. The acid electrolyte is replaced by a strong soln. of an alkali hydroxide or peroxide and the battery is charged in the usual way. If the soln. becomes acid it is replaced by fresh alk. soln.

Electrode for oxidations or reductions. R. H. MCKEE. U. S. 1,433,017, Oct. 24. A pervious, adherent, acid-resisting coating such as infusorial earth and Na silicate is applied to a conductive base which may be formed of Pb in order to increase the efficiency of the electrodes, e. g., in reducing $Na_2Cr_2O_7$.

Grid electrode for electron discharge devices. J. H. PAYNE, JR. U. S. 1,432,411, Oct. 17. The electrode comprizes a relatively large helix of fine wire associated with smaller helices at least one turn of which is interposed between every adjacent pair of turns of the larger helix.

Electrode mounting for apparatus for electrolytic treatment of cloth. A. O. TATE. U. S. 1,432,220, Oct. 17.

Electric battery. F. M. HOLMES. U. S. 1,433,136, Oct. 24. A compn. for use in primary or storage batteries as an electrolytic mixt. is prepd. by treating bone meal with H_2SO_4 , removing free H_2SO_4 from the product by washing with H_2O , drying the product and mixing it with silica flour, fuller's earth or kieselguhr and a compn. prepd. by treating $PbCO_3$ with H_2SO_4 .

Electric battery. W. HOPPIE. U. S. 1,432,025, Oct. 17. Electrolyte material is contained in cartons placed between flat electrodes in the battery cell and the battery is rendered active when desired by crushing the cartons by pressure of a cam which acts on the electrode plates.

Dry cell electric battery. A. S. LYHNE. U. S. 1,432,347, Oct. 17. Battery cups of Zn are formed with a length 2.07 times their diam. in order to afford unusually large area and increased life of the cell as compared to standard sizes.

Dry cell electric battery. O. E. RUHOFF. U. S. 1,432,417, Oct. 17. Structural features.

Hydrometer for electrolytic cells. T. MIDDLEY, JR. U. S. 1,432,773, Oct. 24. A hydrometer is mounted beneath the surface of electrolyte so as to indicate on a scale the d. of the liquid, *e. g.*, in storage batteries.

Electric resistance heating device. W. S. HADWAY, JR. U. S. 1,432,064, Oct. 17. A heating element to which steam is supplied is formed of a mass of carborundum or other insulating particles and concentric Fe tubes the innermost of which serves as a resistor.

Electric furnace. T. S. CURTIS. U. S. 1,433,448, Oct. 24. A furnace adapted for clinkering magnesite is provided with horizontal electrodes mounted on adjustable carriers and provided with graduated scales to regulate their distance of sepn.

Resistance heater for electric furnaces. E. F. COLLINS. U. S. 1,432,442, Oct. 17. A ribbon-shaped resistor which may be formed of "nichrome" is bent into convolutions which together constitute a self-supporting arch.

Electric heating grid for furnaces. L. T. WEIDRICK. U. S. 1,432,505, Oct. 17. C bricks are arranged in the form of a grid in an elec. circuit with arcing gaps adjacent the grid at its opposite ends. A furnace thus constructed is adapted for melting steel or for other purposes.

Electrode holder for electric furnaces. J. YOUNG. U. S. 1,432,823, Oct. 24.

Electrolytic iron. F. A. EUSTIS, C. R. HAYWARD, H. M. SCHLEICHER and D. BELCHER. U. S. 1,432,543, Oct. 17. A ferric soln. such as anode discharge liquor from Fe deposition is reduced with H_2S , and sulfide ore is leached with the reduced soln. to dissolve the Fe from the ore and liberate H_2S . The H_2S is employed for continuing the process and the leach liquor is utilized for electrodeposition of Fe.

Electrolytic iron. F. A. EUSTIS, C. R. HAYWARD, H. M. SCHLEICHER and D. BELCHER. U. S. 1,432,544, Oct. 17. A ferrous soln. suitable for the electrodeposition of Fe is prepd. by dissolving Fe oxide from oxidized ore in a soln. containing dil. acid and a ferrous salt, *e. g.*, a soln. obtained from treating a ferric soln. with SO_2 .

Electrolyte for refining tin. W. P. THOMPSON. Brit. 185,808, May 31, 1921. An electrolyte for refining Sn consists of an acid, preferably hydrofluosilicic acid, in which Sn is dissolved and to which a relatively small proportion of H_3PO_4 is added to render insol. any Pb contaminating the Sn. The electrolyte is prepd. by intermittently immersing baskets made of impure Sn or hard rubber contg. impure shot Sn in oxidizing tanks contg. a 15.5% soln. of hydrofluosilicic acid until the soln. has taken up 4.5% of its wt. of Sn.; the baskets are then suspended above the tanks until it is necessary to rejuvenate the soln. The soln. is continuously circulated between the oxidizing and the electrolytic tanks by a pump. H_3PO_4 is added before soln. and from time to time during electrolysis; the proportion may be from 0.1 to 0.3%; about 0.1% of cresylic acid, and from 0.05 to 0.1% of glue may also be added. Slabs of impure Sn are used as anodes and sheets of pure Sn as cathodes. Both sets of tanks are lined with asphaltum paint.

Purification and concentration of material containing tungsten, molybdenum or their compounds. R. E. PEARSON, E. N. CRAIG AND DURELCO, LTD. Brit. 185,842, June 11, 1921. Material contg. W, Mo or their compds. is purified and concd. by anodic oxidation. If an acid electrolyte is used the metallic impurities go into soln., leaving the tungstic or molybdic oxide or the metals; if an alk. electrolyte is used the W and Mo go into soln., leaving the impurities. *E. g.*, crude molybdenite is crushed to a fine

powder and made into a paste with the electrolyte, which may consist of dil. H_2SO_4 ; it is supported on an anode plate and may be agitated from time to time. Fe and Al_2O_3 go into soln. and the sulfide of Mo is converted into oxide; the molybdic oxide that remains may be sepd. from the SiO_2 gaug which remains by NH_3 treatment. A voltage of 4-7 v. may be used. In treating wolframite, a 25% soln. of NaOH may be used as electrolyte. The W goes into soln. as Na tungstate, and ferrous and Mn oxides are converted into higher oxides, which remain as a sludge on the anode plate. In treating impure tungsten powder obtained, *e. g.*, by reduction of the yellow oxide with H, H_2SO_4 of sp. gr. 1.2 is used as electrolyte. The paste is introduced into a porous pot in which an anode of Pt wire is inserted. The cathode is a stout rod of Pb. A current density of 5 amp. at 5 v. is used. The current density at the anode is kept low to prevent excessive oxidation of the W. It is stated that soda crystallizes out on the cathode. The contents of the anode pot may, after the reaction, be transferred to the cathode compartment of another cell, the cathode in this case being a group of Ni-Cr rods and the anode a rod of Pb. Any W oxidized during the anode reaction is reduced by this treatment, and As and S are removed; sol. SiO_2 passes into the soln. The contents of the cathode pot are washed and dried and reduced by H, and may then be compressed into bars and sintered. Oxalic acid may be used as electrolyte when Na is the main impurity, HCl when Fe is the main impurity, and H_2SO_4 when carbides are present; these electrolytes may be used successively. Cf. 181,837 (C. A. 16, 4148).

Bath for depositing glossy metal coatings on metals. A. CLASSEN. Brit. 186,459, July 14, 1921. A bath for depositing glossy metal coatings on metals, *e. g.*, of Zn on Fe, contains an org. or inorg. colloid or substances forming them and an oxidizing agent capable of preventing the formation of H₂ at the cathode but not powerful enough to decompose the colloids. The following are suitable oxidizing agents, namely, salt-like compds. of H_2O_2 with alkalis, NH_4 or alk. carths; peracids, such as persulfuric and permonosulfuric acids, and persalts such as persulfates, percarbonates, perborates, persulfates and ortho- and pyrophosphates; the urea and other org. derivs. of H_2O_2 ; and under certain conditions H_2O_2 itself. Perchloric acid and perchlorates are unsuitable. The colloid may consist of alum, of starch, albumin or gelatin or their degradation compds. of albumoses or albuminates. A suitable bath contains 10 kg. of ZnSO_4 , 2.5 kg. of $(\text{NH}_4)_2\text{SO}_4$, 120 cc. of H_2SO_4 (1.8° B ϕ), 100-120 g. of alum and 120 g. of K persulfate per 100 l. A current density of 5 amps. per sq. dm. and a pressure of 3 v. are used.

Lixivating zinciferous materials. F. HANSERG. Brit. 186,589, Aug. 9, 1922. Zinciferous materials are lixiviated by a weak acidified electrolyte such as ZnSO_4 led from electrolyzing vessels by a tube opening at the bottom of a tube-shaped extension of a funnel. Undecomposed particles of the stirred-up material settle down and may be removed through a discharge normally closed by a cock, clear neutral electrolyte passing back to the electrolyzing vessels through a pipe. To prevent whirling, the funnel contains partitions which may be conical and concentrically arranged with respect to the funnel. A no. of receptacles may be operated in series.

Ferro-uranium. F. F. MUELLER and R. W. HARRIS. U. S. 1,433,403, Oct. 24. U oxide is heated to a reducing temp. with carbonaceous material in an elec. furnace having a lining mainly formed of non-carbonaceous material such as U oxide and after the temp. has been raised sufficiently to eliminate most of the C from the bath Fe is added to produce ferro-U low in C and Si. U. S. 1,433,404 relates to an *elec. furnace* with a lining formed mainly of U oxide and adapted for use in this process.

Tungsten. GENERAL ELECTRIC CO., LTD. AND C. J. SMYTHILLS. Brit. 186,497, Aug. 23, 1921. In the manuf. of W suitable for elec. lamp filaments, there is added to the W compd., before its reduction to metal, a combination of two substances, one of

which will introduce into the resulting metal au oxide irreducible by H, such as thorja or silica, and the other an alkali metal compd. *E. g.*, there may be left in the tungstic acid before its reduction thorja 0.5–1 and NaCl 0.03–0.3 or Cs chloride 0.05–0.5%, the subsequent reduction, pressing, sintering, swaging, and drawing being carried out in the usual manner. Cf. 155,851 (C. A. 15, 1661).

Electric ozone generator. R. L. JOSEPH. U. S. 1,431,957, Oct. 17.

Arc shield. W. H. KEMPTON. U. S. 1,431,961, Oct. 17. Arc shields are formed partly of a compn. of port. cement, asbestos and H₂O and partly of a mixt. of port. cement, asbestos, carborundum and H₂O, molded together and cured by heating and drying.

"Self-cleaning" electric precipitator for separating suspended particles from gases. H. F. FISHER. U. S. 1,433,266, Oct. 24.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

Complex compounds. A. MAGNUS. *Physik. Z.* 23, 241–7 (1922).—The theories of Kossel (C. A. 10, 2654) are extended to the formation of complexes. By computations based on K.'s formula $U = me^2/r$ (U = energy liberated in formation; e = unit electrostatic charge; r = mean distance of centers of added ions from that of the central atom) values of m are calcd. for halogen complexes in which 1–8 ions are added to central atoms of valence 1–6 and the max. values of m found to correspond with the most stable compds. Octahalogen complexes are indicated as impossible with central atoms of valence 2, 3 or 4 but as the most stable compds. with 5- or 6-valent atoms. That these are rare and confined to fluoro salts is ascribed to expenditure of energy, "energetic hindrance," analogous to steric hindrance, in consequence of which small central atoms or large ions form complexes more difficultly. *E. g.*, C forms no halogen complexes; Si does with F but not with Cl, Br or I. The method of computation is extended to other cases where data are available and the following conclusions are drawn: Formation of mol. compds. is ascribed to the bipolar nature of the added compds. In mol. compds. high coordination nos. are more frequent with relatively small central atoms in consequence of relatively small energetic hindrance which decreases rapidly with the decreasing "screening off" effect at greater distances of atom centers. Bipolar ions, particularly those with higher individual charge and greater bipolar length, are more stably bound than at. or quadripolar (SO₄, PtCl₆, IAg₂) ions and give higher coordination nos. for a given valence of central atom, *e. g.*, CN than halogens. Directed valence forces can generally be disregarded. The structure of electron shells of the central atom requires consideration only rarely. Also in *Z. anorg. allgem. Chem.* 124, 289–321 (1922).

A. R. MIDDLETON

System chromium trioxide-sulfur trioxide-water. L. F. GILBERT, H. BUCKLEY AND I. MASSON. *J. Chem. Soc.* 121, 1934–8 (1922).—A partial survey of the condensed ternary system CrO₃-SO₃-H₂O has been made by carrying out measurements of the soly. of CrO₃ at 25° and 45° in H₂SO₄ of varying concn., accompanied by analyses of the solid phases. Both isotherms are almost coincident. The data show that there are 3 distinct regions, each with a min. of soly. The first region corresponds with CrO₃ as the solid phase. The min. soly., 0.3% by wt., occurs in aq. H₂SO₄ of 70% H₂SO₄ and the transition to the next stage occurs at 85% H₂SO₄. From this concn. to 85% H₂SO₄ the solid phase is CrO₃.SO₃. With higher concns. of SO₃ the third region is entered and the solid becomes probably CrO₃.SO₃.H₂O. The solubilities of the complex compds. are small but give a dark brown color to the liquids. They are extremely hygroscopic

and liberate scarlet CrO_3 on exposure. A table is given showing the variation of the d. of the liquid with its compn.

D. MACRAE

Reduction of thorium oxide by metallic tungsten. RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., LONDON (work conducted by COLIN JAMES SMITHHELLS). *J. Chem. Soc.* 121, 2236-8(1922); cf. *C. A.* 15, 3424; Wedekind, *C. A.* 16, 4147.—A series of gas-filled lamps having W filaments contg. 0.7% ThO_2 were burned for various periods at different temps., and the filaments examd. microscopically and chemically. It was found that as the temp. and time of burning were increased, the residue from soln. of the filament in boiling HF + HNO_3 became green, blue or grey and diminished in vol. After burning at a sufficiently high temp. only a microscopic residue remained and this consisted of grey metallic crystals and contained no particles of thorium. If, however, the filament is volatilized in CHCl_3 and air, a residue of ThO_2 is obtained, showing that a large part of the Th is still in the filament. It is concluded from these expts. that ThO_2 is reduced to Th by W at about 2700° K. There is also evidence to show that the W oxide formed combines with some unchanged ThO_2 to form a Th-W bronze of compn. $\text{Th}(\text{WO}_3)_n$, where n may be from about 3 to 10.

D. MACRAE

A study of calcium carbide. ERLING BOTOLFSSEN. *Ann. chim.* 18, 5-48(1922).—Attempts were made to prep. pure CaC_2 by decompn. of $\text{CaC}_2\text{C}_2\text{H}_5\cdot 4\text{NH}_3$ (A), according to the directions of Moissan (*Compt. rend.* 127, 912(1898)). A was prepd. in glass app. with purified materials. In most of the expts. the heating was carried out beyond 150° (Moissan) and even to 700°. The gases H_2 , NH_3 and C_2H_2 were given off during the heating, the H_2 predominating and increasing in proportion with the time taken for heating. Qual. tests and the gases liberated on adding H_2O indicated the presence of C, CaH_2 , $\text{Ca}(\text{CN})_2$, Ca_3N_2 , and CaCN_2 in the residue, besides the CaC_2 desired. The relative proportions of NH_3 , H_2 , and C_2H_2 liberated on adding H_2O to the residue varied considerably with the conditions of the expt. The prepn. of calcium ammonium ($\text{Ca}(\text{NH}_2)_2$) (B), was carried out between -15 and +30°. A new explosive decompn. of B was noted in vacuum between 34° and 100°, the temp. varying with pressure. The decompn. products indicated were H_2 , CaH_2 and Ca_3N_2 . Treating the residue with H_2O yielded 33% NH_3 and 66% H_2 in nearly constant proportions. This decompn. may indicate a compd., similar to B but contg. less NH_3 , which is formed on decompn. of B above 34°, and the existence of which would establish a series of these compds. The prepn. of CaC_2 from the elements was best accomplished under a pressure of Ca vapor in a sealed Fe bomb, heated at 950° for 45 hrs. This product contained C and Fe to about 1.5 and 1%, resp. The CaC_2 was black, indicating this to be the color of pure CaC_2 . An alundum crucible was attacked, showing the reduction of Al_2O_3 by Ca, observed here for the first time. Other expts. show no proof for the existence of a lower carbide of Ca, but support a dissociation of CaC_2 into the elements at temps. above 1000°. The construction of an elec. vacuum furnace is described, which is adapted for high temp. work.

HENRY C. PARKER

Preparation and properties of trimethylstannane (KRAUSE AND GREER) 10.

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Technical sedimentation analysis. I. FRIEDRICH-VINCENZ V. HAHN AND DOROTHEA V. HAHN. *Kolloid-Z.* 31, 96-101(1922).—The size and form of the app. previously described (cf. Ostwald and Hahn, *C. A.* 16, 3773) was modified so as to make it suitable for use in technical analyses. A study was made of the degree of fineness of soot furnished by different firms; the results agreed with those obtained by other meth-

ods, such as measuring the vol. of material settled out after shaking with some liquid which does not react with the soot, the microscopic method and the use of black standards. This method had the advantage of simplicity of operation and requires less time for measurements.

H. M. McLAUGHLIN

The use of conductivity titrations in precipitation analyses. V. Conductivity titrations with barium salt. J. M. KORTHOFF. *Z. anal. Chem.* 61, 433-8 (1922).—By conductivity measurements it is possible to titrate Na_2SO_4 solns. with BaCl_2 soln. even at considerable diln. In dil. solns. the addition of alc. favors the formation of the BaSO_4 ppt. more than does the addition of a little BaSO_4 . In the presence of mineral acids and Al^{+++} , too little SO_4^{--} is found by conductivity measurements but the presence of Fe^{+++} often causes the opposite result. Ca^{++} causes low results and the disturbance is serious in dil. solns. of SO_4^{--} so that the conductivity method should not be used for the detn. of SO_4^{--} in drinking water. The presence of NO_3^- has little effect in dil. solns. but in concd. solns. too much SO_4^{--} is found; some $\text{Ba}(\text{NO}_3)_2$ is carried down with the BaSO_4 ppt. CO_3^{--} and CrO_4^{--} can be titrated by the conductivity method with BaCl_2 but PO_4^{--} cannot be titrated and P_2O_5 only within about 4%. Solns. of Na oxalate, tartrate, citrate and malate can be titrated with BaCl_2 if sufficient alc. is added but salicylate and benzoate cannot be titrated with accuracy.

W. T. H.

Uses of amalgams in volumetric analyses. V. Estimation of iron, titanium, uranium and methylene blue. SUETARO KIKUCHI. *J. Chem. Soc. Japan* 43, 544-50 (1922); cf. *C. A.* 16, 2818.—Zn-Hg is applied to a mixt. of 2 metallic compds. and each metal is to be estd. by differential titration with 2 different oxidizing agents. (1) *Fe and Ti*.—When the mixt. with the amalgam is reduced, and titrated with iron-alum using NH_4SCN as an indicator, only Ti will be estd., while KMnO_4 oxidizes both. By this method, the amts. found correspond very closely to the theoretical values. Ti can also be estd. by 2N Na tartrate and I. (2) *Fe and U*.—According to Kano (*C. A.* 16, 2818), a reduction of U salt by Cd-Hg in CO_2 gives U^{+++} . Thus by reducing the mixt. of Fe and U by Cd-Hg, and by titrating with KMnO_4 and iron-alum, Fe and U can be estd. (3) *Ti and U*.—K. found that U^{+++} is not oxidized by an excess of I in presence of Na tartrate. Thus if the mixt. is reduced by Cd-Hg in CO_2 , and titrated with KMnO_4 and I, Ti and U can be estd. (4) *Methylene blue*.—A known quantity of Ti salt is reduced to Ti^{+++} by Zn-Hg and titrated with methylene blue (at 60-70°), formation of greenish tint being taken as the end point. The result shows that the original methylene blue was 82.96% pure if calcd. on the basis of $\text{C}_{16}\text{H}_{18}\text{H}_2\text{N}_2\text{S}_2\text{Cl}$ (Kahlbaum methylene blue B extra), or 85.07% if calcd. on the basis of $2\text{C}_{16}\text{H}_{18}\text{N}_2\text{S}_2\text{Cl} + \text{ZnCl}_2 + \text{H}_2\text{O}$ (Merk's methylene blue B. B.). VI. Electrometric titration of iron, molybdenum, uranium, vanadium and titanium. NAOTSUNA KANO. *Ibid* 550-6.—With a view of detecting more accurately the end point of titration of colored solns., K. applied electrometric titration. The metallic salts were first reduced with the amalgam (Zn-Hg), and after each addn. of the oxidizing agent (KMnO_4), the e. m. f. was detd., Pt and calomel electrodes being used. The results with Fe, Mo and V show very close agreement with the theoretical values. In case of U, it was previously shown that presence of air was necessary to convert the salts to U^{+++} by Zn-Hg. The results of electrometric titration of U show that in spite of sharper end point, the error was fairly large (theoretical 0.2028 g.; that found 0.2020 g.). In case where the air interferes with titration, the electrometric method might produce more error than ordinary indicator titration, the former requiring more time than the latter. In all cases, a great increase of the soln. during the titration should be avoided. A mixt. of Fe and Ti could be estd. without using 2 different oxidizing agents (see above) if electrometrically titrated, the curve having 2 sharp reflection points.

S. T.

A new qualitative method for separating the alkaline earth metals. M. POLONOVSKI. *Bull. soc. chim.* 31, 806-10(1922).—The method is based on the relative solubilities of the sulfites and thiosulfites in aq. alc. The carbonates are dissolved in AcOH and after boiling off CO_2 the soln. is neutralized with NH_4OH . Ba is pptd. by the addition of $\text{Na}_2\text{S}_2\text{O}_3$ and alc. The small quantity of Ba^{++} that remains in soln. is pptd. by adding a very little K_2SO_4 . The Sr is pptd. as sulfite by the addition of an excess of $\text{Na}_2\text{S}_2\text{O}_3$ in alc. or as sulfate by means of an excess of K_2SO_4 . The soln. is then made acid with AcOH and the Ca pptd. as CaC_2O_4 . For carrying out the procedure it is important to use the reagents and vols. of alc. exactly as prescribed in the original paper.

W. T. H.

An approximate volumetric method for determining barium. M. POLONOVSKI. *Bull. soc. chim.* 31, 810-3(1922).—The fact that BaS_2O_3 is less sol. than the corresponding Sr and Ca compds. may be used to det. the approx. Ba content of mixts., a standard soln. of $\text{Na}_2\text{S}_2\text{O}_3$ in dil. alc. being used as reagent. After standing about 36 hrs. the BaS_2O_3 is filtered off and the excess reagent detd. iodometrically. A correction factor is given which allows for variations due to temp. and amt. of alc. present, which affect the soly. of BaS_2O_3 .

W. T. H.

The separation of ferric and aluminium oxides from magnesia by the basic acetate method. A. CHARRIQU. *Compt. rend.* 175, 693-5(1922).—Some magnesia is carried down with the Fe and Al in the basic acetate pptn. If the ppt. is heated to about 150° , which is sufficient to cause complete decomposition of Fe or Al acetate, and is then washed with a boiling 4% soln. of AcONH_4 , all but about 1 mg. of the MgO can be removed.

W. T. H.

Volumetric determination of copper based on its precipitation as nitroprusside. GEORGES JORRET. *Ann. fals.* 15, 354-6(1922).—Dissolve an amt. of sample contg. about 0.1 g. of Cu in HNO_3 in a 200-cc. flask, dil. to 100 cc., neutralize with NH_4OH , acidify slightly with HNO_3 or AcOH, add 40 cc. of 0.1 N Na nitroprusside (14.89 g. per l.), make up to vol., and filter, adding talc to facilitate filtration if necessary. To 100 cc. of filtrate in a 200-cc. flask add 20 cc. of 0.1 N AgNO_3 , let stand a few minutes, shake and filter. Titrate the excess of AgNO_3 in 100 cc. of filtrate with KCNS, using ferric alum as indicator. C. P. Cu gave 99.9 and 99.85%, c. P. CuSO_4 99.9 and 99.95%, and "pure" CuSO_4 98.95 and 99.1%. Bi could interfere by partial pptn., but can be eliminated with NH_4OH . Ni, Co, and Ag interfere, being pptd. as nitroprussides. A mixt. contg. Zn, Pb, Sn, Fe, As, Mn, and 50% of Cu gave 49.8, 49.85% Cu. The method was used on a large no. of com. brasses and bronzes and gave results very close to pptn. as CuS and to detn. of Cu by difference.

A. P.-C.

New method for the determination of manganese. ST. MINOVICI AND CONST. KOLLO. *Chimie et industrie* 8, 499-500(1922).—The method is based on the reaction $2\text{HIO}_3 + \text{MnX}_2 = \text{Mn}(\text{IO}_3)_2 + 2\text{HX}$. The soly. of $\text{Mn}(\text{IO}_3)_2$ at room temp. was found to be 0.195% in water, 0.5906% in 1% H_2SO_4 , 0.2800% in 1% HNO_3 , 0.116% in 50% alc., and 0.0050% in 70% alc. It is insol. in 50% or 70% alc. satd. with $\text{Mn}(\text{IO}_3)_2$, and in 70% alc. in the presence of HIO_3 . Heat the soln. of Mn salt on the water bath, add sufficient HIO_3 soln. (about twice as much as is theoretically required for pptn.), heat 10 min. longer on the water bath, cool, add double the vol. of the soln. of 93-95% alc., stir thoroughly, let settle, decant through a tared filter or Gooch, wash first by decantation and then op the filter till free from HIO_3 , preferably with 70% alc. satd. with $\text{Mn}(\text{IO}_3)_2$. 50% or 70% alc. contg. no $\text{Mn}(\text{IO}_3)_2$ can be used, but a correction must be applied for the soly. of the $\text{Mn}(\text{IO}_3)_2$. No Mn could be detected in the filtrate. The errors found on working with a soln. of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ which had been standardized by Volhard's method, as modified by Gooch and Austin, ranged from 0.0002 g. on 0.3128 g. (—0.63%) to +0.0007 g. on 0.0627 g. (+1.11%). The errors are of the same order

of magnitude as with the standard methods. The method possesses the advantages of being quick, accurate and applicable to the detn. of small amts. of Mn. A. P.-C.

Electrometric determination of nickel with silver nitrate. E. MÜLLER AND H. LAUTERBACH. *Z. anal. Chem.* 61, 457-64(1922).—Prepare 0.1 *N* AgNO₃ and standardize an approximately 0.1 *N* KCN soln. against it electrometrically. To 10-20 cc. of the Ni soln. add an excess of KCN and then titrate the excess with AgNO₃ soln. This is done conveniently by making the voltmeter read 0.075 volt at the start and titrating till the galvanometer passes through the 0 reading. Complete directions are given for the proper manipulation of the app. W. T. H.

The gravimetric determination of nickel as nickel dioxide. W. VAUBEL. *Chem.-Ztg.* 46, 978(1922).—The dimethylglyoxime method of Brunck makes use of a relatively expensive reagent so that it is sometimes desirable to det. Ni otherwise. Considerable doubt prevails in the minds of analytical chemists as to the exact compn. of the ppt. obtained by igniting a Ni hydroxide ppt. but there is evidence in favor of the fact that a stable NiO₂ exists and is formed under the conditions that prevail in the following procedure. Ppt. the Ni as Ni(OH)₂ with NaOH in the usual way. Ignite the ppt. and then wash thoroughly to dissolve adsorbed alkali. Ignite again and dissolve the residue in the crucible with HNO₃. Evap. off the excess acid and heat for 30 mins. at 280-330°. Weigh as NiO₂. W. T. H.

Some new methods of volumetric analysis. Determination of sulfate, lead, acid and ammonia. K. JELLINEK AND H. FENS. *Z. anorg. allgem. Chem.* 124, 185-202 (1922).—The theory upon which pptn. methods of volumetric analysis are based is discussed with particular reference to soly. products and the mass action law. As a result of such consideration, a no. of new volumetric methods were devised and tested. (1) *Detn. of sulfate.*—To a fairly dilute soln. contg. about 2 milli-equivs. of sulfate add an excess of 0.1 *N* Ba(NO₃)₂ soln. at the boiling temp. Cool to room temp. and ppt. the excess of Ba⁺⁺ with a slight excess of 0.1 *N* K₂CrO₄ soln. Although there is not a great difference in the soly. products of BaSO₄ and BaCrO₄, there is practically no reaction between the crystalline BaSO₄ produced under the above conditions and the cold CrO₄⁻. Finish the titration by adding 0.1 *N* Ba(NO₃)₂ until a colorless supernatant soln. is obtained. Owing to the difficulty in detecting this condition in the presence of BaCrO₄ and BaSO₄ ppt., it is advisable to have a comparison soln. which has undergone the same treatment but is known to contain an excess of Ba⁺⁺. The results of 7 tests on this method show that the av. error is about 0.05 cc. on 18 cc. of 0.1 *N* soln. About 0.3% too little SO₄ was found. Another series of expts. in which the pptn. of BaSO₄ was effected in more concd. soln. showed a positive error of 0.3%. Attempts to carry out a similar titration with a little Ag⁺ in the soln. so that the end point could be detd. by the color of Ag₂CrO₄ were not as successful. The av. error was 1.13%. (2) *Detn. of lead.*—Excellent results were obtained by the following procedure: Treat about 1 milli-equiv. of Pb(NO₃)₂ at 0.1 *N* concn. with a slight excess of 0.1 *N* K₂CrO₄ in the cold. Add 3 drops of 1% AgNO₃ soln. and 0.1 *N* Pb(NO₃)₂ soln. until no coloration of Ag₂CrO₄ is apparent, using a pure PbCrO₄ ppt. as comparison. The results by this method av. within 0.05% of the truth. The titration is less satisfactory if the end point is taken at the appearance of the Ag₂CrO₄ color. After standing some time, however, the PbCrO₄ ppt. tends to become orange even when no Ag⁺ is present. (3) *Titration of metal ions with arsenate and arsenite solns.*—A series of expts. were performed in the hope of working to a colored arsenite or arsenate and at least 13 different cations were tested in each case but no useful method was evolved. There is not enough difference in the solys. of the colorless and colored arsenates and arsenites. (4) *Detn. of ammonia and acid.*—A sharp end point can be obtained in the titration of acid or of NH₃ solns. by adding 10 drops of 5% CuSO₄ soln. to the acid and titrating with NH₄OH till a blue color is ob-

tained. The method has some advantages over titration with methyl orange but the results are about 1.9% too high for the NH_3 content. By applying a corresponding correction factor the results were good in 5 expts.

W. T. H.

Research on arsenic. A. BULLETER. *Schweiz. Chem.-Ztg.* 1920, 360.—The method of detg. minute amts. of As proposed by B. (cf. C. A. 13, 406) depends upon the distn. of As with H_2SO_4 and NaCl, elimination of the HCl by HOCl and detn. with a Marsh app. The necessity of using the least possible amt. of HCl has suggested the use of gaseous HCl and the replacement of the HOCl by fuming HNO_3 . The HNO_3 soln. can be evapd. without loss of As. Mirrors of the order of 0.01–0.1 μ g. were obtained with the same intensity by the 2 procedures.

C. C. DAVIS

The determination of small quantities of fluorine, particularly in blends and other minerals. ET. OLIVIER. *Rev. universelle mines* 14, 25–49 (1922).—Methods have not heretofore been available for accurately detg. F when present in 0.1% or slightly greater % in blends and other minerals. Two simple, rapid and accurate methods are developed for detg. very small amts. of F. *First method.*—This is based on the relative insoly. in dil HOAc of CaF_2 compared with CaCO_3 and CaSO_4 . A 5 g. sample is digested in 100 cc. of 1% HOAc, filtered and the residue treated successively in this way until only traces of Ca are detected in the filtrate. Three digestions usually suffice. The residue is treated with 30 cc. concd. HCl, then with 10 cc. HNO_3 and evapd. to dryness, and dissolved in HCl. By detg. the Ca by ordinary methods the F. can be calcd. *Second method.*—This is developed in 3 modifications. (1) 1 g. dry powdered sample, 0.5 g. sand and 3 cc. concd. H_2SO_4 are placed in a crucible and covered with a glass plate on the under side of which is a drop of H_2O . If F is present, a white annular ring immediately forms on the periphery of the drop and SiO_2 falls in a funnel-shaped stream to the bottom of the crucible. An annular groove between the white SiO_2 ring and the periphery of the drop of H_2O is etched in the glass. It was proved by sep. expts. that the HF formed momentarily by the action of SiF_4 on the drop of H_2O produced this furrow, thus: $\text{SiF}_4 + 4\text{H}_2\text{O} \longrightarrow \text{Si(OH)}_4 + 4\text{HF}$; $4\text{HF} + 2\text{SiF}_4 \longrightarrow 2\text{H}_2\text{SiF}_6$, and not HF from the action of H_2SO_4 on the fluoride with SiO_2 present. The funnel-shaped stream is caused by the SiF_4 evolved forming, with the vapor of the drop attracted by the dehydrating action of the H_2SO_4 , Si(OH)_4 and H_2SiF_6 according to the reactions above. This new method is superior to previous methods in that (a) F can be detected with SiO_2 present; (b) a Pt crucible is unnecessary; (c) a protective coating on the glass is not used and (d) a quant. detn. of F can be made by the characteristic groove. The annular SiO_2 ring and the etched groove bear a constant relation to each other for a given amt. of SiF_4 evolved, and this can be detd. by a set of standards. Elaborate directions are given for the best conditions and technic. Briefly, the blende must be finely divided; a porcelain crucible of 17 cc. is to be used; finely pulverized sea sand is preferable to glass or quartz; the crucible and sand should be first put in hot concd. H_2SO_4 for 6 hrs.; the H_2SO_4 should have a d. 1.835; the drop of distd. H_2O should be approx. 1/30 cc. and be spread to an area of 15 mm. diam. and by means of a large supply; the same window glass should be used for all tests. By pulverizing a blende contg., e. g., 1% F, in varying proportions with a F-free blende, samples are obtained contg. 0.005, 0.01, 0.02, 0.03, 0.05, 0.1, 0.2 and 0.5% of F. These are then utilized to form at both 18° and 80° a series of samples in which the different intensities of groove and SiO_2 ring are distinguishable. This test is sensitive to 0.0001 g. of F, but is inaccurate for amts. of F in excess of 0.005 g. Blendes with too high % F should be mixed in known proportions with amts. of F-free blende. (2) 1 g. of blende, 0.5 g. of sand and 20 cc. concd. H_2SO_4 are put in a 100 cc. matrass leading by a glass tube to the stem of an inverted funnel. The funnel rests over a drop of H_2O 15 mm. diam. on a pane of glass. Surrounding the drop are several drops of concd. H_2SO_4 to dessicate the air, so that

the SiF_4 reaches the drop in a dry state. The reaction mixt. is heated to 160° . The results can be compared as before with a set of standards. This method is limited to 0.005 g. of F for the annular SiO_2 ring and to 0.00005 for the groove. (3) The reaction mixt. is the same as in (2), and is heated at 160° , but differs in that a current of dry air carried all SiF_4 and SO_2 through a tube 1 cm. diam. into 50 cc. distd. H_2O , or better in a U-tube contg. 10–20 cc. H_2O . At the surface of the H_2O an annular ring of SiO_2 is formed, the mass and appearance of which are proportional to the amt. of SiF_4 . Since all F is in soln. in this SO_2 soln. as H_2SiF_6 and HF , the test for F may be made more delicate by evapg. at 80° drops of this soln. on glass. A characteristic annular groove is left by each drop. The soln. can be dild. until the visible limit of this groove is reached. An amt. of chloride should be used to give a SO_2 soln. contg. at least 0.002 g. of F. Solns. do not visibly corrode glass when the F is less than 0.00033%. This test is extremely sensitive, for a drop contg. 0.0000001 g. of F. gives a faint but visible groove. Tests on numerous common reagents showed that only NH_4OH and certain soft waters attack glass similarly to HF . Emphasis is thus laid on the necessity for blank tests for all methods. *First method* also in *Rass. min.* 57, 42–3(1922). C. C. D.

Determination of available chlorine in chlorine bleaching compounds. F. DIENER and F. WANDENBULCKE. *Ann. fäls.* 15, 338–9(1922).—Dil. 1 cc. of the bleaching soln. to 1 l., add 2 g. of $(\text{NH}_4)_2\text{SO}_4$, shake, and add a few crystals of KI and some starch soln. Titrate the liberated I with an alk. As_2O_3 soln., 1 cc. of which = 1 mg. of available Cl. The $(\text{NH}_4)_2\text{SO}_4$ prevents the formation of iodate. The method was compared with those of Penot, Poncius, and Gay-Lussac, and all of them gave approx. the same results, Poncius' method always giving slightly higher results than the others. Especially with low Cl contents, Poncius' method gives high results, depending on the rate of addition of the KI soln., because the reaction between KI and KIO_3 does not take place instantaneously. Penot's method is not suitable for very dil. solns. A. P.-C.

Conductometric titration of fluosilicic acid. NAOTSUNA KANO. *J. Chem. Soc. Japan* 43, 556–60(1922).—By using a large beaker, a stirrer and 2 adjustable, parallel Pt plates as electrodes, it was found possible to get good results in the titration of H_2SiF_6 by the conductometric method. With 100 cc. of water and about twice as much alc. as solvent for the 0.14 N acid, it was found possible to get good results with either NaOH or KOH and hydrolysis caused no trouble. S. T.

The use of benzidine as a sensitive test for phosphoric acid. F. FÉGL. *Z. anal. Chem.* 61, 454–7(1922).—To det. whether a filtered and washed yellow ppt. produced by $(\text{NH}_4)_2\text{MoO}_4$ actually contains P, moisten it with benzidine hydrochloride soln. to which a little AcOH has been added. Then hold the filter and ppt. over an open ammonia bottle. If P_2O_5 is present the yellow ppt. will turn blue. By means of this test it is possible to detect in 10 cc. of soln. 1 part of P_2O_5 in 300,000 of H_2O . Since hexavalent Mo gives blue reduction products and benzidine yields blue oxidation products it is probable that the effect of the P_2O_5 is to catalyze an oxidation-reduction reaction between the Mo and benzidine. In carrying out the test the $(\text{NH}_4)_2\text{MoO}_4$ soln. should be freshly prepared and a good grade of quantitative filter should be used as Fe compds. on the filter may give rise to a coloration with benzidine. W. T. H.

The titration of nitrous acid and the determination of nitrous and arsenious acids in the presence of one another. A. KLEMENC. *Z. anal. Chem.* 61, 448–54(1922).—Instead of titrating H_3AsO_3 with KMnO_4 in an open vessel it is better to place the KMnO_4 in a flask with about 1/3 as much 60% H_2SO_4 , displace the air with CO_2 , add the As soln., heat for 5 mins. in a bath at 40° and then titrate the excess KMnO_4 with oxalic acid. When H_3AsO_3 and HNO_2 are both present in a soln., the former can be titrated with I_2 in the presence of excess NaHCO_3 and then both HNO_2 and H_3AsO_3 titrated with KMnO_4 . Some difficulty was encountered in getting the same results

with KMnO_4 and I_2 in the case of H_3AsO_2 but this difficulty was overcome by using a considerable excess of KMnO_4 and a fairly high acidity. About 1/6 as much 75% H_2SO_4 as 0.1 N KMnO_4 is recommended. A careful study of oxidation potentials and application of the Nernst equation show that the titration of H_3AsO_2 by I_2 in the presence of HNO_2 would hardly be expected to give accurate results. It appears almost accidental that such a titration does succeed and is probably due to the fact that there is considerable reaction resistance to the oxidation of HNO_2 by I_2 ; it is probably necessary to form as primary product some of the so-called "per-nitric" acid which requires a higher potential.

W. T. HALL

The complete quantitative analysis of ammonia as a lecture experiment. P. RITSCHBIETH. *Z. physik. chem. Unterricht* 35, 134-5(1922).—A measured vol. of NH_3 is burned with CuO , the evolved N_2 is measured and the vol. of O_2 required to change the reduced Cu back to CuO is detd.

S. MORGULIS

Detection of pyridine. FRIEDRICH LEHNER. *Chem.-Ztg.* 46, 877(1922).—To the soln. to be tested add a little water and a trace of CNBr (preferably freshly prepd.), then a few drops of aniline. The soln. immediately becomes red and crystals of α -anilinophenyldihydropyridine bromide sep. With 1 part pyridine in 350,000 the soln. is colored yellow, after about an hr. orange, and after 2-2.5 days, reddish oily drops appear.

E. H.

The analysis of mixtures of hydrogen with the paraffin hydrocarbons. R. WIGGINSON. *Fuel* 124, 152(1922).—Comments on a method presented by King (*C. A.* 16, 3600) for removing H and CO from their admixt. with paraffins by fractional combustion. On account of certain difficulties of the method, it is suggested that the reaction between CH_4 and CuO be accelerated by the use of CuCl as catalyst (cf. *J. Chem. Soc.* 12, 48(1896)).

C. C. DAVIS

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

Silicates of strontium and barium. PENTTI ESKOLA. *Am. J. Sci.* 4, 331-75 (1922).—Considering the wide occurrence of isomorphous sulfates and carbonates of Ca, Sr and Ba, the question rises: Do Sr and Ba under exptl. conditions form such silicates as are known in the case of Ca? For this study the purest SiO_2 , Ca, Sr and Ba carbonates obtainable were used. These substances were dried at 150° , weighed, mixed, melted if possible, chilled and crushed, then reheated and ground twice more. The equil. relations were ascertained by the quenching method. Heating curves were run in some cases for the purpose of checking the temp. measurements. Temps. were detd. by a potentiometer and a thermoclement calibrated against the m. p. of diopside and anorthite. Refractive indices were detd. by the improved immersion method of Merwin. The systems $\text{SrO} \cdot \text{SiO}_2$, $\text{BaO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{SiO}_2$ - $\text{SrO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$ - $\text{BaO} \cdot \text{SiO}_2$ were worked out and the results collected in 12 tables and 12 charts of curves. Crystallographic features are shown in 5 illustrations. Sr and Ba feldspars were found to be analogous to anorthite.

L. W. R.

Ishikawaite, a new mineral from Ishikawa, Iwaki province. YUJI SHIBATA AND KENJIRO KIMURA. *J. Chem. Soc. Japan* 43, 648-9(1922).—The crystallography of the "unnamed mineral from Ishikawa" (*C. A.* 16, 2825) confirmed it to be a new mineral, which is named *ishikawaite*. It shows $a:b:c = 0.9451:1:1.147$; and the forms: c (001), a (100), g (210), h (320), m (110), n (140), b (010), r (144), and d (101).

S. T.

Mineralogy of three gouge clays from precious metal veins. E. V. SHANNON. *Proc. U. S. Nat. Museum* 62, No. 15, 11 pp.(1922).—Ore-bearing veins of the "true-fissure" type, whether the ore has developed by filling of open cavities or by replacement

of wall rock adjacent to fissures, in the majority of instances are accompanied by more or less clayey material commonly called selvage, talc or clay gouge. This material would be expected to have the compn. of the walls, but is generally radically different. This paper deals with gouge materials from 3 Idaho Au and Ag veins. *Leucierite* gouge from Black Jack mine, Owyhee Co. resembled hard soap, pale pink on the outside, white within and no grit when tested between the teeth. Microscopic examn. showed the material to be entirely cryst. with $ns. \alpha = 1.488$, $\gamma = 1.513$, sepg. it from sericite and kaolinite. The compn. was: SiO_2 45.32, Al_2O_3 27.84, Fe_2O_3 0.70, CaO 2.76, MgO 0.16, K_2O 0.12, Na_2O 0.10, $H_2O + 110^\circ$ 8.16, $H_2O - 110^\circ$ 14.48, sum 99.64% which yields the approx. formula $Al_2O_3 \cdot 3SiO_2 \cdot 5H_2O$. *Sericite* from the Carroll-Driscoll mine, Boise Co. is cream or dirty white to pale green in color, foliated with silky luster. Its $\alpha = 1.550$, $\beta = 1.585$, $\gamma = 1.587$, and compn.: SiO_2 46.58, Al_2O_3 37.46, Fe_2O_3 0.80, CaO trace, MgO 1.16, K_2O 6.38, Na_2O 0.64, $H_2O + 110^\circ$ 6.06, $H_2O - 110^\circ$ 0.30, sum 99.38% which yields the formula $(H,K)_2O \cdot Al_2O_3 \cdot 0.2SiO_2$ with H and K replaced to a slight extent by Mg. A sample of *clay* from Garfield Tunnel, DeLamar district, was greenish or pink on the outside and white within. The $\alpha = 1.547$, $\gamma = 1.556$, and compn.: SiO_2 45.94, Al_2O_3 34.14, Fe_2O_3 1.26, CaO 0.84, MgO 0.18, K_2O 6.52, Na_2O 0.18, $H_2O + 110^\circ$ 7.00, $H_2O - 110^\circ$ 2.70, sum 98.76%, which resembles kaolinite but differs by lower $ns.$ and by the mol. of H_2O released at 110° . The compns. of these clays yield important information as to the character of the vein-forming solns. L. W. RIGGS

An occurrence of impsomite in West Australia. R. F. FARQUHARSON. *Chem. Eng. Mining Rev.* 14, 407-9 (1922).—The mineral is black with a brilliant luster, brittle and seamed with cracks, ignites freely, and does not melt on heating to 300° . Its $d. = 1.154$; calorific value, 16,573 B. t. u. Proximate analysis gives: 0.37% moisture, 41.54 volatile constituents, 56.27% fixed C, 1.82% ash. The volatile matter consists of 1.74% H_2O , 19.89% oil, 19.91% gas. It occurs in fractures, and vesicles in basalt sheet, and was probably formed by distg. of hydrocarbons from a carbonaceous shale.

W. H. N.

The Lower Silesia copper deposits. F. BEYSLAG. *Z. prakt. Geol.* 5, 67-73 (1918).—Chalcopryite, bornite, chalcocite, tetrahedrite, native copper, malachite and azurite are the ore minerals. Quartz predominates as a gang mineral. A porphyry magma was probably the source of the ores.

W. H. NEWHOUSE

The lignin origin of coal, a geologic and palaeontologic impossibility. R. PORONIN. *Braunkohle* 21, 365-9 (1922).—Exception is taken to the theory of Fischer and Schrader (cf. *C. A.* 15, 1610, 3202, 3548, 3899; 16, 3538) that lignin is the essential substance from which coal is formed and that cellulose is destroyed. Based on the chem. evidence alone, this theory might be justified, but many geologic and palaeontologic facts tend to disprove it. Various investigations show lignin to be in too low % in the plants from which coal is derived to be the chief source of coal. Cellulose has not always been destroyed, and is shown to be present in certain deposits. No lignite or fossil cellulose has been found with evidence of bacterial destruction of cellulose (cf. Jeffrey, *C. A.* 5, 1330). Decompn. products not only of lignin but also of cellulose are present in humus coals. A bibliography is included.

C. C. DAVIS

The origin of bituminous coal and anthracite. JOHN ROBERTS. *Colliery Guardian* 124, 459-60, 517-20, 593-4 (1922).—A discussion of the theories of the formation of coal seams. A crit. examn. and comparison of data and theories of numerous investigators have led to the conclusions: (1) anthracite (A) must have been derived from a coal substance very low in ash; (2) the materials most likely to have entered into its original compn. were clairain (B) and vitrain (C); (3) conchoidal fracture is closely related to jelly-like substances such as are characteristic of pure coal ingredients like B and C; (4) a pure, bright, caking coal can be converted into a coal having luster, volatile and ash

contents of A by heating in the region of 600°; (5) it is very improbable that infusible and difficultly fusible durain formed part of the original A except in small proportions; (6) the depth of a seam in the coal measures determines to a limited extent its state of anthracitization; (7) folding, faulting and a high temp. of the strata cause a reduction in the % of volatile in coals; (8) iridescence in a coal has probably been caused by the action of heat driving off some of the volatile from coals in the neighborhood, a thin film of C or hydrocarbon being deposited on the "peacock" coal; (9) the metamorphic and selective deposition theories must be combined to explain the origin of A; (10) evidence points to the theory that A results from the metamorphism of pure, bright coal, probably both B and C; (11) the behavior of A when subjected to thermal distn. suggests that it has previously attained a temp. approx. 500° *in situ* and (12) the temp. of metamorphism of bituminous coal into A lies in the region of 500°. C. C. DAVIS

Basic rocks of the massive of nephelite syenite of "Serra de Monchique" and of their environs. PEREIRA DE SOUSA. *Compt. rend.* 175, 698-701(1922).—Thirteen chem. analyses with parameters by Raoult are quoted, and form the basis of this study. Under the biotite series the interrelations between the shonkinites and theralites are described. In the hornblende series the similarity of these rocks to the berondrites of Madagascar is shown, the extreme type of the series being a feldspathic wehrlite. The rocks of the series with basaltic facies are to be considered as microberondrite with alk. feldspars. They form a small outcrop in the syenite. L. W. RIGGS

Rocks rich in barium. Geol. Survey, New S. Wales, *Mem.* 8, 337(1922).—A remarkable rock type has been found in the vicinity of Broken Hill, N. S. W. It is fine grained, grayish white, and looks not unlike an aplite. It appears to consist mostly of feldspar, with a few thin parallel streaks of a darker mineral. Its sp. gr. is high. Analysis shows over 9% BaO. The Ba is probably contained in the feldspar, but calcu. shows that there is not enough Al_2O_3 present to satisfy the feldspar formula, assuming all Ba and Ca to be in the feldspar. The mineral is not identified. O. P. R. O.

Exchange of the substances of the earth. V. M. GOLDSCHMIDT. *Z. Elektrochem.* 28, 411-21(1922).—A discussion of the probable compn. of the earth and the exchange of its components. From the results of astronomical, geodetical, seismological and petrographical investigations, it is deduced that for a depth of 120 km. from the surface the earth consists of a shell of silicate having a d of 2.8. Beneath this, extending to a depth of 1200 km. from the surface, lies a shell of compressed silicates of $d = 3.6$ to 4. Extending to a depth of 2900 km., next comes a layer which consists chiefly of sulfides of Fe, containing also O compds. of Fe, Cr and Ti corresponding to the troilite-chromite nodules of meteorites, and a series of heavy metals such as Cu, Ag, and Au. Below this shell lies the actual nucleus of the earth. This consists most probably of Ni-Fe, containing about 6-10% Ni. Its d is about 8. The exchange of substances between the different shells, and the action of erosion, sedimentation, etc., at the earth's surface are discussed. H. JERMAIN CREIGHTON

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

Little known difficulties occurring through sulfur troubles in blast furnace practice. A. KILLING. *Stahl u. Eisen* 42, 968-78(1921).—When the S in blast furnace slag becomes higher than 3% difficulty is met with infusible masses forming in front of the tuyères. R. S. DEAN

Determination of heat losses in metallurgical furnaces. L. FAHRNICH. *Elektrotech. u. Maschinenbau* 39, 597-9(1921); *Science Abstracts* 25B, 310.—Comments on Rosin's paper (C. A. 15, 2406). The detn. of heat loss as the difference between heat

supplied and that theoretically necessary is unsatisfactory and does not allow distinguishing between different sources of loss. The calcn. preferred is based on $Q = kF(T_1 - T_2)/d$, in which F is the cross section of brickwork of thickness d ; T_1 and T_2 the temp. of inner and outer surfaces, resp.; and t the time required for the operation per unit charge.

LOUIS JORDAN

Powdered coal for malleable iron. I. T. W. ATTERBURV. *Foundry* 50, 815-9 (1922).—The advantages of powd. coal over band firing in melting or annealing malleable Fe are cleanliness, low coal consumption, saving in labor, less scrap in pouring, a more uniform product, heats are tapped on time, capacity of the furnace is increased, less repairs to brick lining and better working conditions. Expts. on a 28-ton furnace bear out these advantages. The coal should be ground so that 85% passes a 200-mesh screen and should contain 1% or less moisture. The coal feeding equipment is thoroughly discussed and the control method with automatic CO_2 recorders is explained.

C. H. HERTV, JR.

The metallurgy of semi-steel. DAVID McLAIN. *Iron and Steel of Canada* 5, 206-10 (1922).—M. claims that C acts as a medium through which other elements work. Steel absorbs C in the cupola up to 5% but this is not necessarily the predominating element as it is impossible to produce chill castings with 2.75% Si. It is believed that Si is the controlling element. A casting with 2.75% Si will contain the C almost entirely in the graphitic state and the casting will be soft, while a casting with 1.75% Si will be hard, with 0.5% combined C. Semi-steel exceeds in temp. and fluidity any other mixture made in the cupola; oxidation is scarcely perceptible; carbonization of the steel charged begins at a low temp. and increases rapidly as the temp. rises. No special appliances are necessary as the same cupola is used for both grey iron and for semi-steel and the operation is very flexible as to the time that the steel is charged. Wedge test for castings of different sections consists in casting into a wedge-shaped pattern 16 in. long, 2 in. square at one end, tapered to a feather edge 2 in. wide. This shows great difference in microstructure at different sections. Semi-steel gives the most homogeneous wedge. Medium P and low Si give the best qualities to semi-steel. Scientific melting together with generalities are given. Annealed semi-steel gives excellent results in castings.

C. H. HERTV, JR.

Gold metallurgy of the Witwatersrand (Transvaal). W. CULLEN. *J. Chem. Soc. Ind.* 41, 316-21 (1922).—A description of the new plant and operations of the New Modderfontein Gold Mining Co., together with a discussion of past progress and possible future improvements on the Rand. Since 1903 the percentage of Au extn. has been raised from 90 to 95. Tailings now carry only 1 s. per ton. Cost of plant in 1903 was £215 per ton of ore treated; this was cut in half by 1914, but is now as high as in 1903. Expts. with flotation appear promising. This suggested use of tube-mills exclusively instead of stamps would cut capital costs and reduce gold thefts. In the early days slimes could not be leached, but they are now treated more cheaply and yield higher extn. than the sands. In general it pays to grind as fine as possible. The consumption of cyanide in 1894 was 1.2 to 2.0 lb. per ton of ore; now it is about $1/10$ as much. Solns. were formerly 0.3 to 0.6% KCN, now $1/5$ to $1/10$ as strong. Consumption of Hg has been reduced from 4 oz. per ton of ore to 0.1 oz. C. also discusses the chemistry of cyanide soln. and pptn.

A. BUTTS

New treatment plant of the United Comstock mines. GEO. J. YOUNG. *Eng. Mining J.-Press* 114, 846-53 (1922).—A detailed description of operations and equipment at the newest and largest cyanide mill in the Western States. The plant, located at Virginia City, Nev., is of steel and concrete construction. The Ag-Au ore contains considerable wood and is high in sol. salts; it is therefore given a preliminary coarse crushing and washing in warm water, which separates the salts and a primary slime con-

taining the wood pulp. The latter is screened out and the slime thickened, filtered and cyanided. The coarse washed ore is fine ground in cyanide soln., and the sand and slime are separated and further treated.

A. BUTTS

Beilby's theory of the amorphous phase of metal. CARL BENEDICKS. *Rev. metal.* 19, 505-13(1922).—A review of Beilby's recent book. After reviewing each chapter separately B. lists six objections to Beilby's conclusions. In support of the objections B. states his theory of hardness: *viz.*, pure metals are not hard; hardness is due to impurities which cause different "slip-planes" in a single crystal upon cold working.

W. A. MUDGE

Overstrain, internal stresses and creep. ZAY JEFFRIES AND R. S. ARCHER. *Chem. Met. Eng.* 27, 833-7(1922).—Fe is hardened much more by working in the blue heat range than at certain lower temps. This behavior may be a general property of metals and has been observed in Ni and certain alloys. These phenomena and the results of overstrain are all due to rapid acquisition of increased strength on slip planes. The elastic limit of Fe is lowered sometimes to 0 by cold-working, but is restored by aging or heating at low temps. to a value which may be much higher than its original value.

V. O. HOMERBERG

Properties of cold-worked metals. ZAY JEFFRIES AND R. S. ARCHER. *Chem. Met. Eng.* 27, 882-9(1922).—Hardness and strength of a metal increase with the amt. of reduction by cold-work until internal failure is produced. Plasticity of a metal decreases as the amt. of cold-work increases. With change in temp. of test, the properties of a cold-worked metal follow those of annealed metal, any discontinuities in the properties of annealed metal being reflected in those of cold-worked metal. The effect of a given deformation is greater the lower the temp. at which it is effected, except that in some metals abnormally large effects are produced in a certain region of temp., corresponding to the blue heat in Fe. Elongation of a cold-worked metal increases with respect to the elongation of annealed metal, as the temp. of test decreases below the working temp., reaching a max. value, after which further decrease in temp. produces a rapid decrease in elongation. Elongation of a cold-worked metal decreases with respect to the elongation of annealed metal as the temp. of test is raised above the working temp. until the recrystallization temp. is reached, when elongation is increased by annealing. Temps. of max. elongation are different for various metals. For any given metal, the temp. of max. elongation is lower the greater the amt. of cold-work, and is in general lower in cold-worked metal than in annealed metal. In metals which become brittle on cooling because of intercrystalline weakness, the cold-worked metal may possess considerable elongation at temps. at which the equi-axed metal is brittle. The greater the amt. of cold-work the less is the elongation at the temp. of working or at the temp. of max. elongation on cooling. The hardening effects of slight or moderate deformations are greater the smaller the initial grain size of the metal. Reduction of area of a cold-worked metal is in general less than in the annealed state. The properties of cold-worked metals are explained by a series of postulates regarding conditions at the slip planes. A general theory is checked by expts. on Cu, Ni, Fe, Mo and W.

V. O. HOMERBERG

Mechanical properties as affected by grain size. ZAY JEFFRIES AND R. S. ARCHER. *Chem. Met. Eng.* 27, 789-92(1922).—Grain boundaries add a certain stiffness to the metallic aggregate. Fine grain therefore generally involves higher tensile strength and hardness, and greater reduction of area. Max. elongation requires medium grain size.

V. O. HOMERBERG

The thermal improvement of automobile motors. HELLER. *Arch. Warmewirtsch.* 3, 67-70(1922).—The higher heat cond. of *light alloys* enables higher compression without pre-ignition to be used in engines whose pistons are of this material. Their

thermal efficiency is thus increased. Sixteen alloys of Al or Mg were used as pistons in a motor truck engine, the max. compression without pre-ignition, and the capacity and efficiency being detd. Charts are given of the results, which show that the best alloys produce a 20% increase in power and 20% decrease in fuel consumption.

ERNEST W. THIELE

Tests on high-tin bearing metals. P. W. PRIESTLEY. *Chem. Met. Eng.* 27, 928-31 (1922).—High-speed gas engines require bearings of highest quality. General remarks are given on the chem. compn. and the microstructure of suitable alloys. Detailed directions for casting in bronze shells are given. A series of commercial alloys were tested for hardness, compressive strength, and coefficient of friction. Bearings were also run dry until destroyed.

V. O. HOMERBERG

Effect of electrode size on metal deposition (in arc welding). D. N. LOUIS. *Elec. World* 80, 888 (1922).—The size of the electrode used in arc welding should be such that the current in them is about 8000 amp. per sq. in. If the electrodes are too large the arc is harder to maintain, the rate of deposition is slower and the penetration is excessive. If the electrodes are too small they are fused too rapidly, with the result that the metal is deposited before the parent metal is fused, causing poor penetration and large overlap. The proportions between the size of the electrodes and the current density for most successful results on work of average size are 90 to 125 amp. for Fe electrodes 0.125 in. in diam. and 150 to 200 amp. for 0.2 in. electrodes. C. G. F.

Electrodes for copper, bronze and brass welding. ANON. *Electrician* 89, 485 (1922).—The metal core is of pure Cu surrounded by a flux covering [compn. not divulged] which adheres firmly to the rod. The temp. range between the welding and fusing temp. of Cu, brass and bronze is very short and care must be taken not to pierce the work. C. G. F.

The Greenawalt electrolytic Cu extraction process (GREENAWALT) 4. Applications of electric equipment in the metallurgy of nickel (YARDLEY) 4. Optical constants of sodium-potassium alloys (MORGAN) 2. Experiments on structure with X-rays (KIRCHNER) 2.

Sintering of roasting ores in continuous operation. A. S. DWIGHT. U. S. 1,433,348-9-50-1-2-3-4-5, Oct. 24. Mech. features of ore treatment on a continuously moving carrier.

Lead and silver from ores. H. HAY. U. S. 1,432,858, Oct. 24. Products contg. Ag and Pb as chlorides are leached with a hot brine contg. FeCl₃ or other chloridizing reagent so rapidly as not to allow time for reversion of the AgCl. U. S. 1,432,859 relates to preferential chloridization of Pb and Ag in sulfide ores, followed by successive leaching with cold brine to ext. Ag and with hot neutral brine or other solvent for Pb remaining in the Ag-free residue.

Treating copper-nickel solutions. H. G. C. FAIRWEATHER. Brit. 185,859, June 15, 1921. Cu is pptd. by means of finely divided Ni from solns. contg. Cu and Ni at a temp. below that of exhaustion of the Ni. Bessemerized Cu-Ni mat may be ground, roasted, and leached with H₂SO₄; part of the leached residue is reduced to metal and is used in excess as a precipitant for the soln. obtained from the remainder of the leached residue, the pptn. being carried out at normal temps., and preferably on the counter-current principle. The Cu-Ni powder with the Cu cemented thereon is roasted, preferably in admixt. with roasted or unroasted mat. In the sepn. of Ni and Cu by electrolysis, the Ni sulfate electrolyte contg. H₂SO₄ may be supplied to the cathode compartment and passed through a filtering diaphragm to the anode compartment, the impure Ni-Cu soln. formed being drawn off, purified as described above, and returned to the cathode compartment.

Zinc retort and portable fume condenser. A. DONALDSON. U. S. 1,432,842, Oct. 24.

Furnace adapted for producing steel. H. R. GRIFFITHS. U. S. 1,433,452, Oct. 24.

Composition for coating steel to protect it during hardening. A. BRICKLEY. U. S. 1,432,523, Oct. 17. Fire-clay 1, "Cil-o-cel" or other light fibrous material 1, dry SiO_2 1 and a soln. of Na silicate 3 parts.

Protective coating for metals. J. H. YOUNG. U. S. 1,432,512, Oct. 17. Metal articles such as sheets for building purposes are coated with hard asphalt, a layer of felt impregnated with a fire-resisting mixt. of asphalt and chlorinated C_{12}H_4 , with a overlying layer of relatively hard asphalt. Cf. C. A. 16, 2766.

Cleaning metals. L. J. G. DE BURLANT and V. L. J. BÉGUER. Brit. 186,338, Sept. 19, 1922. Metal articles, prior to tinning, galvanizing, etc., are cleansed in a concd. soln. of a double chloride of Zn and NH_4 at a density of not less than 35°Bé . which is kept boiling (110°) during immersion of the articles. The bath is regenerated by means of thin Zn strips which are dipped into it to ppt. the Fe, etc., in soln. Articles may be left to dry up to 24 hrs. before galvanizing or 6 hr. before Pb coating or tinning. The cleaning process may be accelerated by a preliminary immersion of the articles in dil. HCl.

Alloys. ALLGEMEINES DEUTSCHES METALLWERK GES. Brit. 186,336, Sept. 18, 1922. Bronze alloys consist of not less than 87 parts of Cu, 4.5-10 parts of Sn, 1-5 parts of Ni, and not more than 5 parts of Zn. The Cu and Ni are first melted together, the Sn is then added, and finally the Zn.

Alloys. ALLGEMEINES DEUTSCHES METALLWERK GES. Brit. 186,337, Sept. 18, 1922. A Cu-Zn alloy having less than 40% of Zn contains also Ni, Mn, and Fe, and not more than 3% of Al. The alloy may consist of 40-55 parts of Cu, 8-15 parts of Ni, 1-3 parts of Mn, 1-2 parts of Fe, 0.5-3 parts of Al, and less than 40 parts of Zn. The Cu, Ni, Mn, and Fe are first melted together, the Zn is then added, and finally the Al.

Alloys. W. JONES and SYLVETTE, LTD. Brit. 186,381, May 26, 1921. 1-3% of Al and 2-4% of Fe are added to a Ni-Ag alloy. A small proportion of a deoxidizer may be added, e. g., 0.5-1% of Mn or a small quantity of Mg. The alloy is suitable for making spoons and forks by casting in a horizontal position.

Ferro-chromium alloy. W. B. HAMILTON and T. A. EVANS. U. S. 1,432,269, Oct. 17. A rust-resisting alloy is prepd. by melting Fe or steel so as to provide a layer of slag over it and then adding to the slag a Cr oxide ore in the presence of a thermo-reducing agent such as Al, Si or Mg to reduce the oxide and liberate Cr which unites with the molten Fe beneath the slag.

Copper-nickel-zinc alloy. F. MILLIKEN. U. S. 1,432,607, Oct. 17. An alloy adapted for being forged or worked cold is formed of Cu 60-70, Ni 9-12, Zn 19-24, Fe 1-2.5% and a small amt. of Mn.

Heat-resisting alloy. A. H. COPLAN. U. S. 1,433,180, Oct. 24. An alloy of Fe adapted for the manuf. of furnace grate bars is formed with a content of Cr 1%, Ni 2%, Mn 0.60% or more, C 0.10% or more and small amts. of S and P.

Treating iron to prevent rusting. C. W. PORTER. U. S. 1,433,226, Oct. 24. A soln. for rustproofing Fe is formed of amyl amine 5-10, NaOH 10-15 and H_2O 1000 parts.

Solution for quenching and carburizing metals. FRED PALMER and FRANK PALMER. U. S. 1,433,408, Oct. 24. Na_2SO_4 2 oz., NaCl 8 oz., $\text{K}_4\text{FeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$ 2 oz., and H_2O 1 gal.

Case-hardening metal articles. H. RODMAN. U. S. 1,432,416, Oct. 17. Articles such as gears to be case-hardened are packed in a non-coking material such as coke

granules above an underlying layer of uncoked coking material such as coal and lime and these materials are all heated together in a carbonizing box to a carbonizing temp.

Apparatus for pickling metal sheets or plates. H. S. THOMAS and W. R. DAVIES. U. S. 1,432,578, Oct. 17. Arms attached to a horizontal rotating shaft carry metal plates beneath the pickling soln. as the shaft rotates.

Brass tubing. D. L. SUMMEY. U. S. 1,432,803, Oct. 24. Wrought billets are formed of Pb-free brass contg. over 62.5% Cu and tubes are then formed from the billets by hot rolling.

Forging metal blanks. E. D. LOWELL. U. S. 1,433,213, Oct. 24. Blanks of steel are protected from scale formation by enclosing the blank in a close-fitting envelope of electrodeposited Ni or other ductile metal which has a higher m. p. than the temp. to which the blank is to be heated, and working the heated blank while it is protected by the envelope.

Bearing metals. T. GOLDSCHMIDT AKT.-GES. Brit. 186,058, Sept. 12, 1922. Addition to 172,003 (C. A. 16, 1068). The alloys described in the principal patent are improved by the further addition of 0.5-5% of one or more of the metals Cd, Bi, Tl, and Hg.

Acid-proof casting. H. TERRISSE and M. LEVY. U. S. 1,432,923, Oct. 24. Castings of good mech. strength and high resistance to acids are formed of Fe alloyed with Si 10-30% and W 2-20%. A small % of V may also be added.

Electric welding rods and soldering sticks. E. H. JONES and ALLOY WELDING PROCESSES, LTD. Brit. 185,813, June 3, 1921. Electrodes, welding rods, and soldering sticks used for depositing metal by means of the elec. arc contain ferro-carbon or silicon-carbon alloy, the min. % of C being 20% in the former case and 25% in the latter.

10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

The absorption of ethylene by sulfuric acid. The production of ethyl alcohol, of diethyl sulfate and of liquid hydrocarbons. A. DAMIENS. *Compt. rend.* 175, 585-8 (1922).—It has already been shown that it is possible to prep. EtOH (A) on an industrial scale by the catalytic absorption of C_2H_4 (B) in H_2SO_4 (C) (cf. C. A. 14, 1115). Data are now given for this reaction, other than catalytic. The rate of absorption is directly proportional to the pressure and to the surface of contact. Agitation is very important, 12,000 agitations per hr. increasing the absorption 20-7 times. Addn. of 2 parts of H_2O per 100 to the concd. C reduced the rate to 0.5. Raising the temp. favored absorption, but above 60° a partial decompn. of the org. compds. by the acid occurred. The catalyzer giving the highest rate of absorption was Cu_2SO_4 (D) or $CuCl$. By varying the conditions with these catalyzers, 3 different products were obtained, A, Et_2SO_4 (E) and an oil with all the properties of petroleum. With 1-5 parts of D per 100 in the C at a low temp. $EtHSO_4$ (F) was formed, giving on hydrolysis almost a quant. yield of A. Using acid contg. under 97% C, continued absorption beyond a definite concn. of F caused the formation of E. With 100% C at 15°, the concn. of F in equil. with E was 35.6 parts per 100. On raising the temp. or by dilg. the acid, the equil. was displaced in the direction to destroy the E. The highest yield of E was 17 g. from 17 g. B and 100 g. of C. By carrying out the B absorption in the cold in the presence of D and Hg or Hg_2SO_4 the rate was greatly increased and an oily mixt. of hydrocarbons sepd. with d. 0.77 and with fractions boiling as follows: 110-200°, 40%; 200-15°, 20%; 215-300°, 40%. The average C/H ratio was: complete oil, 5.69; 110-200°, 5.50; 200-215°, 5.59; 215-300°, 5.81. The reactions are assumed to include 2 steps. (1) A complex, $Cu_2SO_4 \cdot n(C_2H_4)$, partially sol. in C is formed, and since

this is stable only in concd. C, diln. of the C causes decompn. and liberation of B. Thus 40 cc. of C having absorbed 1400 cc. of B liberated on diln. 220 cc. of B. (2) The complex is attacked by C, forming either E and F or liquid hydrocarbons. The soln., from which B is liberated on diln., liberated less and less upon standing, and after some hrs. none could be obtained; indicating the 2 steps above. Catalysts other than Cu salts acting alone formed E and F, but hydrocarbons when Hg was present. They were all less efficient than Cu salts.

C. C. DAVIS

Acetylene in technical chemical syntheses. ANON. *J. Soc. Chem. Ind.* **41**, 189-92R (1922).—A review of the methods available for the production of AcH , C_2H_2 , EtOH , C_2HCl_3 , $\text{CH}_3\text{ClCO}_2\text{H}$, HCN and various condensation products from C_2H_2 . The com. application of most of these processes depends upon cheap CaC_2 .

G. W. STRATTON

Preparation of 1,4-dihalogen derivatives of butane. C. S. MARVEL AND A. L. TANENBAUM. *J. Am. Chem. Soc.* **44**, 2645-50 (1922).—A series of reactions has been developed so that $(\text{CH}_3\text{CH}_2\text{Br})_2$ can be obtained much more readily than by the older methods. From 1 kg. $\text{CH}_3(\text{CH}_2\text{Br})_2$ and 370 g. PhOH in 2 l. H_2O refluxed 5-6 hrs., 150 g. NaOH in 500 cc. H_2O being run in during the course of the 1st hr., are obtained 340-80 g. $\text{CH}_3(\text{CH}_2\text{Br})_2$, b_{10} below 136° , 560-600 g. $\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{Br}$ (A), b_{10} $136-42^\circ$, m. $7-8^\circ$, and 50-70 g. $\text{CH}_3(\text{CH}_2\text{OPh})_2$; 1 kg. A, 325 g. NaCN , 325 cc. H_2O and 500 g. of 95% alc. refluxed 15-20 hrs. yield 675-725 g. of the cyanide, b_{10} $162-6^\circ$, m. $41-2^\circ$, 500 g. of which, refluxed about 7 hrs. in 625 g. of 95% alc. and 300 g. H_2SO_4 (d. 1.84), gives 495-516 g. $\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$, b_{10} $160-5^\circ$; 100 g. of this in 150 cc. abs. alc. (distd. from Na) added in the course of 3-4 min. to 10 g. Na in 250 cc. PhMe (the Na is previously broken up into very small particles by heating the PhMe until the Na melts and stirring) in a flask provided with a long (2 m.) and wide (2.5 cm.) reflux condenser, then treated in the course of 12-5 min. with 500 cc. abs. alc. gives 50-4 g. $\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (B), b_{11} $162-4^\circ$, n_D^{25} 1.520, whose *p*-nitrobenzoate m. 91° . In the same way octyl alc., b_{10} $103-5^\circ$, is obtained in 67-75% yield from *Rt* caprylate, lauryl alc., b_{10} $143-6^\circ$, in 65-70% yield from *Et* laurate, myristyl alc., b_{10} $170-3^\circ$, m. $39-9.5^\circ$, from *Et* myristate in 63-75% yield, and $\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, b_{17} $146-8^\circ$, from $\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{CN}$ in 80-7% yield. B (36 g.), 115 cc. HBr (d. 1.48) and 25 cc. H_2SO_4 (d. 1.84) boiled gently 1 hr. and then refluxed vigorously 8 hrs. give 13-20 g. $(\text{CH}_3\text{CH}_2\text{Br})_2$, b_{10} $81-5^\circ$, and 19-20 g. *phenoxybutyl bromide* (C), b_{10} $153-6^\circ$, m. 41° . From 46 g. C refluxed 9 hrs. with 100 cc. HBr are obtained 12 g. $(\text{CH}_3\text{CH}_2\text{Br})_2$ and 32 g. unchanged C. If it is desired to prep. the C only it can be obtained in 50 g. yield from 52 g. B in ice treated with 33 g. PBr_3 in portions, allowed to stand a few hrs. and heated on the H_2O bath. Refluxed 12 hrs. with 120 cc. HI (d. 1.70), 38 g. B gives 18.5 g. $(\text{CH}_3\text{CH}_2\text{I})_2$, b_{10} $147-52^\circ$, and 43 g. $\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$, b_{10} $165-72^\circ$, m. $43-4^\circ$; 43 g. of the latter refluxed 7 hrs. with 60 cc. HI gives 12 g. unchanged iodide and 34 g. $(\text{CH}_3\text{CH}_2\text{I})_2$.

C. A. R.

A synthesis of β -chloroallyl chloride. A. J. HILL AND E. J. FISCHER. *J. Am. Chem. Soc.* **44**, 2582-95 (1922).—Crude $\text{HOCH}(\text{CH}_2\text{Cl})_2$ (A), b. $176-9^\circ$, is obtained in 87% yield from glycerol (dehydrated 2 hrs. at 160°) and 6% AcOH satd. at 100° with HCl ; 200 g. added with const. stirring to 75 g. NaOH in 150 cc. H_2O at $12-5^\circ$ gives 60% epichlorohydrin, b. 117° , 300 g. of which, slowly treated in the cold with 320 g. concd. HCl , yields 80% pure A, b. 177° . When 2 mols. POCl_3 and 3 mols. A are digested 8 hrs. at 100° and 5 hrs. at 180° and dists. *in vacuo*, nothing dists. over, if no unchanged POCl_3 is left, until the temp. reaches 225° , when the phosphoric esters formed as intermediate products decomp. and there is obtained 75% β -chloroallyl chloride (B), oil with a CHCl_3 -like odor, b. $107-9^\circ$. Attempts to prep. B with P_2O_5 instead of POCl_3 under various conditions gave at best only 40% B, and no B was ob-

tained with sirupy H_3PO_4 , anhyd. $(\text{CO}_2\text{H})_2$, KHSO_4 , H_2SO_4 , B_2O_3 , anhyd. ZnCl_2 , I or PCl_5 . B can be used for the alkylation of malonic esters. Thus, *diethyl chloroallylmalonate*, pale yellow oil with the characteristic pleasant odor of malonic esters, n_D^{20} 1.61–3°, b 255–75° (some decompn.), is obtained in 26% yield from 4.2 g. Na in alc., 29 g. $\text{CH}_2(\text{CO}_2\text{Et})_2$ and 22 g. B. *Diethyl di(chloroallyl)malonate* (9 g. from 14.5 g. $\text{CH}_2(\text{CO}_2\text{Et})_2$, 4.2 g. Na and 22 g. B) pale yellow oil, b_D^{20} 190°, b 300° (partial decompn.). *Diethyl ethyl(chloroallyl)malonate* (7 g. from 3.1 g. Na, 25 g. $\text{EtCH}(\text{CO}_2\text{Et})_2$ and 15 g. B), n_D^{20} 157–60°.

C. A. R.

Oxidation of 1,4- and 1,5-oxides. ADOLF FRANK, FRITZ LIEBEN AND SUSI GLAUBACH. *Monatsh.* 43, 225–36(1922).—The oxidation of oxides not only enables one to differentiate between two oxides (isomeric or identical) but also enables one, in some instances, to discover the constitution of the oxides. This in turn will decide whether, in the action of H_2SO_4 upon glycols, a ring contraction has taken place. The oxidation of 1,5-pentanediol gave only $(\text{CH}_2)_5(\text{CO}_2\text{H})_2$; the same acid is obtained from 1,5-oxido-pentane. 1,4-Oxidopentane, on the other hand, gave AcOH and $(\text{CH}_2)_4(\text{CO}_2\text{H})_2$, as did 1,5-oxido-hexane. The oxidation of 1,5-oxido-5-methylhexane gave a lactone, $\text{C}_7\text{H}_{14}\text{O}$, oily, b 220–5°, with a characteristic smell. A little AcMe and $(\text{CH}_2)_5(\text{CO}_2\text{H})_2$ also were formed.

C. J. WEST

New method for the introduction of an ethyl group. The reaction between organomagnesium halides and diethyl sulfate. HENRY GILMAN AND RACHEL E. HOYLE. *J. Am. Chem. Soc.* 44, 2621–6(1922).— Et_2SO_4 reacts with many organomagnesium compds. according to the scheme $\text{RMgX} + \text{Et}_2\text{SO}_4 \longrightarrow \text{REt} + \text{Et}(\text{XMg})\text{SO}_4$. Below are the substances which have been prepd. in this way and the % yields. PhEt , b 134–6°, 83; $p\text{-EtC}_6\text{H}_4\text{Me}$, b 160–1°, 45; PhPr , b 155–6°, quant.; $\alpha\text{-C}_{10}\text{H}_7\text{Et}$, b 256–9°, 70.5; hexane, b 68°, 69.4; ethylcyclohexane, b 128–30°, 80.3; $p\text{-EtC}_6\text{H}_4\text{OMe}$, b 199–200°, 89.4; $\text{PhC}:\text{CEt}$, b 198–201°, 70.3; Ph_2CHOEt (from PhMgBr with BzH and then with Et_2SO_4), b 282–4°, 35.7; Ph_2COH (from PhMgBr , Ph_2CO and Et_2SO_4), 92.3% (only a small amt. of the Et ether, m 53–4°, was formed); BzOEt , b 210–1°, 17.3; *N*-ethyl-*N*-phenylbenzohydrylamine, b 191°, d_4^{20} 1.06, n_D^{20} 1.597, obtained in 90.5% yield from PhCH:NPh and PhMgBr .

C. A. R.

Chloromethanesulfonic acid, $\text{ClCH}_2\text{SO}_3\text{H}$. R. DEMARS. *Bull. sci. pharmacol.* 29, 425–31(1922).—12.95 g. CH_2ClBr and 25.5 g. of $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ in 200 cc. H_2O , are gently heated for 6 hrs. under a reflux condenser; the liquid is evapd. to dryness in a porcelain dish and extd. with EtOH , giving $\text{ClCH}_2\text{SO}_3\text{ONa}$, a white hygroscopic compd., sol. in H_2O , alc. (hot or cold) from which it could be obtained in crystals. The Ba salt was prepd. from ClCH_2Br and KCNS , the product of which reaction, ClCH_2SCN , was oxidized to $\text{ClCH}_2\text{SO}_3\text{H}$ by fuming HNO_3 and pptd. out as $(\text{ClCH}_2\text{SO}_3)_2\text{Ba} \cdot \text{H}_2\text{O}$.

F. S. HAMMETT

Some derivatives of butylarsine and butylarsonic acid. J. TIPPENHAU. *Bull. sci. pharmacol.* 29, 440–2(1922).—When HgBu_2 is mixed with AsCl_3 or PhAsCl_2 various As compds. are produced. From the 1st CH_3AsBu is obtained: from this $\text{O}:\text{AsBu}$ can be prepd. by the use of aq. Na_2CO_3 or K_2CO_3 . The oxide cannot be distd. without decompn. Butyldichloroarsine is a dense colorless liquid, b 175–80°, d_4^{25} 1.54. When it is treated with HNO_3 , butylarsonic acid, $\text{BuAsO}(\text{OH})_2$, is formed, needles, m 138°, sol. in H_2O and alc., insol. in Et_2O . Phenylbutylchloroarsine, PhBuAsCl , formed when HgBu_2 and PhAsCl_2 are allowed to react, is a clear liquid with d_4 1.35. F. S. H.

The preparation of methylmercuric acetate and the isolation of methylmercuric hydroxide. W. C. SNYDER AND J. L. MAYNARD. *J. Am. Chem. Soc.* 44, 2942–7(1922).— MeHgOAc (A) was prepd. in 4 ways, each of which gave a 95–7.5% yield: (1) From Me_2Hg in MeOH with $\text{Hg}(\text{OAc})_2$; (2) from MeHgOH in MeOH with glacial AcOH ; (3) from MeHgOH in H_2O refluxed with AcOEt ; (4) from MeHgI in MeOH with AgOAc .

It is also formed in small amt. in the thermal decompn. of HgOAc in N_2 . It seps. from AcOH in thin satiny platelets, m. 128° , very sol. in H_2O , AcOH and EtOH , while the product described by Otto (*Ann.* 154, 199(1870)) under the same name seps. from AcOH in thin rhombic platelets, m. $142-3^\circ$, practically *insol.* in boiling H_2O and cold AcOH . It possesses a disagreeable odor, sublimes very readily (being slightly volatile even at the temp. of boiling Et_2O) and gives rise to a persistent taste far back in the mouth when handled as such or in soln. for a short time. The methylmercuric hydroxide used in the prepn. of A by 2 of the above methods was made from MeHgI in MeOH with moist Ag_2O ; it m. 95° , and is a strong vesicant, even dil. solns. producing blisters in a few hrs. C. A. R.

Preparation and properties of trimethylstannane. CHAS. A. KRAUS AND W. N. GREER. *J. Am. Chem. Soc.* 44, 2629-33(1922).—Na in liquid NH_3 in a bath of boiling liquid NH_3 treated with very nearly 0.5 equiv. Me_3SnCl quant. gives sodium trimethylstannide, Me_3SnNa ; if, now, it is treated with 1 equiv. NH_4NO_3 it gives trimethylstannane (A) which seps. as an oily liquid. The operation is carried out in a special app. which is described and after the reaction is over the excess of NH_3 is pumped out and the A distd. over *in vacuo* into a weighing tube in a bath of boiling liquid NH_3 . The weighing tube is then allowed to come to room temp., any excess of liquid A in it distd. back by cooling the reaction chamber in liquid NH_3 and the d. of the A vapor detd. by weighing the tube. The value found was 165.53. A reacts with Na in liquid NH_3 and with concd. HCl according to the equations $\text{Me}_3\text{SnH} + \text{Na} = \text{Me}_3\text{SnNa} + \text{H}$ and $\text{Me}_3\text{SnH} + \text{HCl} = \text{Me}_3\text{SnCl} + \text{H}_2$. It is slightly sol. in H_2O and b. 60° . C. A. R.

Action of sodammonium on hexamethylenetetramine, tetramethyldiaminomethane and ethyldieneethylimine. PICON. *Compt. rend.* 175, 695-8(1922).—(NaNH_2), (A) is without action on hexamethylenetetramine (B) even in an autoclave at ordinary temp. Ferrand (*Thesis in Pharmacy, Paris 1920*) has shown that the diverse hydrogenation studies of B have been carried out in alk. or acid media and the hydrolysis of B into CH_3O and NH_3 has resulted. The negative action of A on B in NH_3 soln. is of interest with regard to the constitution of B. Either the action is in accordance with the satd. compd. proposed by Duden and Scharff (1895) or with the unsatd. compd. of Delépine. In studying the action of A on N compds. in this regard, P. could not employ ketimines because all of the compds. prepd. thus far contain a cyclic radical and P. and Lebeau (*Compt. rend.* 175, 223(1922)) have shown that the hydrogenation of an ethylenic linkage by means of A is not effected in the acyclic series, but the reduction may be effected if the bond is adjacent to a ring. Consequently compds. having a cyclic ring were eliminated and fatty imines were chosen. The latter polymerize rapidly but Henry (*Rec. trav. chim.* 23, 401(1904)) has shown that this tendency is diminished as the mol. wt. is increased. Ethyldieneethylimine (C), b. 48° , was prepd. by condensing AcH with EtNH_2 . C is attacked by A in an autoclave at ordinary temp. The reaction product is treated with Et_2O to sep. NaNH_2 and the ext. is distd. in a vacuum. Diethyl-diaminobutane (D), b. $166-7^\circ$, was then found. The hydrochloride is deliquescent, sol. in H_2O and in alc. The sulfate sublimes at 280° , is sol. in H_2O , insol. in alc. A hydrated chloroplatinate was prepd. as were the chloroaurate and chloromercurate. D is a sec. amine and gave with HNO_2 a dinitro derivative, prisms, m. 74.5° , sol. in alc. and Et_2O . With MgEt_2 in Et_2O D gave C_6H_6 . It is shown that when A acts on C, H_2 is added to the N of the imine and then the sec. amine formed condenses by the union of the bond set free on the adjacent C atom. No NH_3 is liberated: $2\text{C}_4\text{H}_9\text{N} + \text{N}_2\text{H}_4\text{N}_2 = 2\text{NH}_3 + \text{C}_6\text{H}_6\text{N}_2$. The action of A on a satd. compd. was studied. $\text{CH}_3(\text{NMe}_2)_2$ is not attacked by A in an autoclave at ordinary temp. after a contact of 24 hrs. The behavior of A towards B indicates that the latter has no double bond between the N and the C atom and this inactivity supports the formula (satd.) proposed by Duden and Scharff.

H. E. WILLIAMS

Laboratory preparation of acetaldehyde. E. WERTHEIM. *J. Am. Chem. Soc.* **44**, 2658-9 (1922); cf. Adams and Williams, *C. A.* **16**, 409. —By stirring the reaction mixt. with CO_2 and using a large condenser in whose jacket H_2O at about 5° is circulated so that the reaction can be run rapidly, $\text{AcH} \cdot \text{NH}_3$ is obtained in 70-2% yield from 25 g. alc. treated with a mixt. of 115 g. HNO_3 (d. 1.42), 60 g. $\text{Na}_2\text{Cr}_2\text{O}_7$, 20 g. H_2SO_4 (d. 1.84) and 220 cc. H_2O at such a rate that a thermometer near the top of the condenser reads $20-5^\circ$; the introduction of the oxidizing mixt. usually requires about 20 min. and the boiling is continued another 10 min. C. A. R.

Decomposition of aliphatic ketones. ALPHONSE MAILHE. *Bull. soc. chim.* **31**, 863-7 (1922). —Using a catalyst composed of Al_2O_3 and Cu, at $600-50^\circ$, M. studies the decompn. of aliphatic ketones (cf. *C. A.* **16**, 3870). The products are almost entirely gaseous, the % of CO , C_2H_4 , C_3H_6 (exclusive of CH_4), CH_4 , and H_2 , resp., varying within the following limits: 18.9-30.9%; 17.2-43.1%; 12.5-35.3%; 7.6-23.5%; 3.7-28.5%. The ketones studied were MeCOCHMe , $\text{MeCOCH}_2\text{CHMe}$, MeCOBu , $\text{MeCO} \cdot \text{Am}(\text{iso})$, $\text{Bu}_2\text{CO}(\text{iso})$, $\text{Me}_2\text{CHCOBu}(\text{iso})$, and $(\text{C}_6\text{H}_{13})_2\text{CO}$. Only in the last case was there evidence of extensive decompn. of the olefin originally formed. B. H. N.

The catalytic decomposition of acids and ketones. A. MAILHE. *Mat. grasses* **14**, 6223-5, 6247-8 (1922). —Results are given of an investigation into the decompn. of aliphatic acids and ketones at $600-650^\circ$ in the presence of Cu- Al_2O_3 as catalyzer. *AcOH* at 600° gave a small amt. of Me_2CO with abundant evolution of gases consisting of CO_2 43.3, CO 12.6, CH_4 18.9, H 25.2%. *Isobutyric acid* at 600° gave a liquid contg. a small amt. of *isobutyron*e and volatile and highly inflammable compds. The gases consist of CO_2 26.7, CO 18.5, C_2H_4 10, C_3H_6 13.3, CH_4 6, H 25%. Brominating the gas gave $\text{MeCHBrCH}_2\text{Br}$. *Butyric acid* gave gases consisting of CO_2 20, CO 12.3, C_2H_4 5.7 (mostly *propylene*), C_3H_6 28.2, CH_4 2.42, H 9.4%. *Isovaleric acid* below 600° gave unchanged *isovaleric acid*, a small amt. of *isovaleron*e, H_2O , and traces of inflammable unsatd. compds. The gases given off consist of CO_2 28.9, CO 17, C_2H_4 10 (largely *isobutylene*), C_3H_6 12.7, CH_4 5, H 26%. *Pelargonic acid*, at $600-620^\circ$, gave a considerable amt. of liquid unsatd. compds. distg. below 150° , and gases consisting of CO_2 20, CO 11.5, C_2H_4 8.5, C_3H_6 25.5, CH_4 11, H 23%. The liquid distg. below 150° contains unchanged *pelargonic acid*, and *nonylone*, easily sepd. as shining needles, m. 48° . Hydrogenation of this liquid with a Ni catalyzer gave a colorless liquid, inactive with Br and H_2SO_4 , partly sol. in fuming HNO_3 , and consisting of a mixt. of aromatic and of aliphatic hydrocarbons. *Oleic acid* gave water, gases with high illuminating power consisting of CO_2 6.7, CO 10, C_2H_4 10, C_3H_6 38, CH_4 11, H 23%, and a liquid contg. lower acids, and a mixt. of aliphatic and aromatic hydrocarbons. *Linoleic* and *linolenic acids* give similar results. *Acetone* at $600-650^\circ$ gave a small amt. of unchanged Me_2CO and gases consisting of CO 15, CH_4 30, H 55%. *Isobutyron*e at 650° gave CO 30.9, C_2H_4 39 (mostly *propylene*), C_3H_6 15, CH_4 11.1, H 3.7%. *Isovaleron*e at 600° gave CO 23.4, C_2H_4 8.6 (*isopropylene* and *isobutylene*), C_3H_6 34.3, CH_4 27.1, H 6.3%. The difference in proportion of C_2H_4 and C_3H_6 in the case of *isobutyron*e and *isovaleron*e is partly due to the difference in the temp. of decompn. *Isopropyl isobutyl ketone* at 600° gives CO 26.8, C_2H_4 15.3 (C_2H_4 , *propylene*, *isobutylene*), C_3H_6 35.3, CH_4 11.3, H 11.3%. *Enanthone* (dihexyl ketone, $(\text{C}_6\text{H}_{13})_2\text{CO}$) gave a small amt. of a volatile unsatd. liquid, and gases consisting of CO 21.4, C_2H_4 43.5 (C_2H_4 , *propylene*, *butylene*, and higher homologs), C_3H_6 13.6, CH_4 7.4, H 13.6%. *Methyl isopropyl ketone* gave CO , *propylene*, CH_4 , H and C . *Methyl isobutyl ketone* at $590-600^\circ$ gave CO , *isobutylene*, CH_4 , H and C . *Methylbutyl ketone* at 630° gave CO , CH_4 , and 33% of C_2H_4 (C_2H_4 , *butylene*, and especially *propylene*). The difference between this and the preceding case is ascribed to the difference in the temp. of decompn. *Methyl isoamyl ketone* was prepd. by catalysis from a mixt. of AcOH

and of methylpentanoic acid, which was itself prepd. by means of iso-AmMgBr. At 630-650° it was practically completely decompd. into gases consisting of CO 20.1, C₃H₆ 39.2 (propylene, isobutylene, and isoamylene), C₃H₈+16.7, CH₄ 7, H 16.7%. The results show that on decomp. acids at 600-650° in the presence of Cu-Al₂O₃, the ketones formed are decompd. as fast as they are generated, the radicals combined with the CO splitting off and breaking down to give both satd. and unsatd. hydrocarbons. The higher the temp. the smaller the no. of C atoms in the products of decompn. With acids higher than those with 7 C atoms unsatd. liquid hydrocarbons are formed.

A. P.-C.

Action of epichlorohydrin on neutral sodium phosphate in aqueous solution and the stability of a diglyceromonomophosphate. O. BAILEY. *Bull. soc. chim.* 31, 848-62 (1922); cf. C. A. 15, 1884.—When a soln. of Na₃PO₄ is allowed to react with epichlorohydrin, a complex mixt. is formed. A large part of the product yields on hydration Na α-glycerophosphate. The remainder consists of a diglyceridophosphate which hydrates to sodium α,α-diglyceromonomophosphate, PO(ONa)[OCH₂CH(OH)CH₂OH]₂ (A), a Na salt of an α,γ-monoglyceromonomophosphate, PO(ONa)[OCH₂CH(OH)CH₂O] (B), and an α,γ-monoglycerodiphosphate. A and B were found to display a remarkable stability. B. was unable to isolate any pure compds.

J. B. BROWN

Ketenes. XI. Keteneacetals. H. STAUDINGER AND G. RATHSAM. *Helvetica Chim. Acta* 5, 645-55 (1922); cf. C. A. 16, 1077.—An investigation of various keteneacetals, 1st as the ethers of methylenecarbonic acid (cf. below) and 2nd as more stable derivs. than the ketenes. *Phenylketene acetal* (A) has been prepd. from MeCCl₂ and 3 mols. PhOK and its carboxylic ester, (EtO)₂C:CHCO₂Et, from NCC₃H₇CO₂Et. With H₂O the ester forms CH₂(CO₂Et)₂ but shows no tendency to polymerize at ordinary temp. Neither A nor its corresponding homologs could be prepd. by S. and R. by the reaction of 1.5 mols. P₂O₅ on MeC(OEt)₂, EtC(OEt)₂, or HC(OEt)₂, which yielded EtOAc (83%), EtOPr and HCO₂Et (90%). Heating the ortho esters with Ni as catalyst was similarly unsuccessful. A can be prepd. from *triethyl orthophenylacetate* (C), PhCH₂C(OEt)₃. The latter was prepd. under anhyd. condition by the action of 50 g. PhCH₂C(OEt):NH.HCl (D) with 60 g. abs. EtOH. After 5 days' standing NH₄Cl was pptd. with Et₂O, the filtrate, after concn. and crystn. of PhCH₂CONH₂ was distd. *in vacuo*. C, colorless oil, b₃₄ 80°, b₁₂ 142°; with H₂O, it decomp. immediately to PhCH₂CO₂Et (D), b_{6.1} 72°. 15 g. C distd. repeatedly under 12 mm. yields 6 g. A (b₁₂ 136°); distd. under 760 mm., it yields A and D. A is more stable than its ketene, polymerizes after 6 hrs. at 260-70° in a bomb tube, yielding D, b₁₂ 108-10°, and a colorless solid, m. 136-7°, also found on decompn. of C. With O₂ at 100° it forms D; with O₂, PhNH₂, and PhNHNH₂ in the cold it does not react; it absorbs Br₂ in CS₂, forming PhCHBrCO₂C₆H₅, b₁₂ 150°. A adds 2 mols. Ph₂C:CO on heating 2 days at 60°, forming colorless crystals, C₁₉H₁₈O₆, probably PhCH₂C(OEt)₂.CO.CPh₂.CO (E),

from EtOH, m. 138°, mol. wt. 542. On sapon. E yields an acid, not investigated further. Attempts to synthesize *diphenyl ketene acetal* from Ph₂CHC(OEt):NH and from Ph₂C:CCl₂ with EtONa were unsuccessful. On distg. the latter mixt. over a free flame, the fraction b. 200-300° consists of tolan, and CH₂Ph₂. Unsuccessful attempts were made with imino esters and phenols; aromatic substituted imino esters could not be prepd.; imino esters could not be made to react with mercaptan. The *acetal of di-*

phenylmalonic ester aldehyde, Ph₂C $\begin{matrix} \diagup \text{CO}_2\text{Et} \\ \diagdown \text{CH(OEt)}_2 \end{matrix}$ (F), prepd. by heating 1 mol. Ph₂C:CO

with 1 mol. HC(OEt)₂ in CO₂ at 60° for 14 days, colorless crystals from low boiling gasoline, m. 58°, depresses the m. p. of Ph₂CHCO₂Et (m. 57-58°), sol. in the usual org. solvents. F dists. unchanged in small quantities, is not affected by alc.

KOH, PhNH_2 or PhNHNH_2 and is hydrolyzed quant. by HCl to $\text{Ph}_2\text{CHCO}_2\text{Et}$ and HCO_2H . **XLI. Derivatives of methylenecarbonic acid.** H. STAEDINGER AND P. MAYER. *Ibid* 656-78.—An investigation of the 3 types of derivs. of methylenecarbonic acid (A), viz. esters, ester salts, and normal salts, to compare the influence of the substituents on the ethylene linkage. That these substances actually are intermediates between the ketenes and the fatty acid derivs. of which they are the enolic forms, is substantiated by their instability, demonstrated here: $\text{R}_2\text{C}:\text{C}:\text{O} + \text{HOH} \longrightarrow \text{R}_2\text{C}:\text{C}(\text{OH})_2 \longrightarrow \text{R}_2\text{CHC}(\text{O})\text{OH}$. This relationship explains the impossibility of obtaining ketenes by simple dehydration of the satd. acids. Prepn. of normal esters is described above. Potassium ethyl diphenylenecarbonate, $\text{Ph}_2\text{C}:\text{C}(\text{OK})\text{OEt}$ (B), may be prepd. in 3 ways. (1) By heating $\text{Ph}_2\text{CHCO}_2\text{Et}$ (C) with 3 mols. EtOK ; as B is unstable to heat it is largely destroyed, but its presence can be demonstrated by alkylation. (2) By the reaction under anhyd. conditions of C on KNH_2 (D) in liquid NH_3 under a stream of N_2 . A new method for the prepn. of D consists in dissolving 0.5 g. K in 50 cc. NH_3 and evap. the latter under a stream of N_2 . The residue is heated in stream of NH_3 at $150-80^\circ$ $1\frac{1}{2}$ hr. Reaction may be completed by redissolving and re-evap. the NH_3 . The addn. of 2.5 g. $\text{Ph}_2\text{CHCO}_2\text{Et}$ forms $\text{Ph}_2\text{CHC}(\text{OK})(\text{NH}_2)\text{OEt}$, which can be sepd. as a yellow salt by the addn. of Et_2O . By prolonged heating in *vacuo*, this forms C. With O_2 in the cold, no peroxide can be isolated, hut on the addn. of H_2O , Ph_2CO and benzoic acid sep. With MeI , followed by sapon. with alc. KOH, $\text{Ph}_2\text{CMeCO}_2\text{H}$, m. $109-72^\circ$, is formed. (3) The best method, by the reaction on 2 g. K powder under C_2H_2 of 15 g. C in 80 cc. Et_2O . B seps. as a white powder which decomp. with H_2O , forming C. On heating the original reaction mixt. 0.5 hr. with 11 g. $\text{Ph}_2\text{C}:\text{CO}$ (E), dilg. and acidifying, CO_2 is evolved, $\text{Ph}_2\text{CHCO}_2\text{H}$ is pptd., and from the coned. residues 6 g. $(\text{Ph}_2\text{CH})_2\text{CO}$ (F), m. 135° , and 2 g. $\text{Ph}_2\text{C}:\text{C}:\text{CPh}_2$ (G) m. 163° (Br deriv. m. 165°), can be sepd. by EtOH . By the reaction of 1 or 2 mols. of E on EtOK [or MeOK], a mixt. of B and $\text{K}_2\text{C}(\text{CO}_2)_2$ is formed which oxidizes immediately to F and G. If the mixed salts are filtered, and oxidized with O_2 or dry air, benzoic acid is found, hut no Ph_2CO . Attempts to isolate the peroxide, working at -80° , were unsuccessful. By the action of EtI on the mixed salts, is obtained $\text{Ph}_2\text{CEtCO}_2\text{Et}$, $b_p 137-40^\circ$, identified by sapon. to the acid, m. 172° . PhOK and E, when treated with MeI , yield $\text{Ph}_2\text{CMeCO}_2\text{Ph}$, $b_p 78-85^\circ$. The tendency to enolization on the part of the normal salts of the fatty acids is slight. Attempts to prep. the normal salts of A by heating the salts of the CO_2H acids with KNH_2 or EtOK were unsuccessful. By the action of $\text{Ph}_2\text{CHCO}_2\text{K}$ on KNH_2 in liquid NH_3 under anhyd. conditions in a N atm. $\text{Ph}_2\text{C}:\text{C}(\text{OK})_2$ (H), is formed, and can be isolated by vacuum drying as a yellow powder which could not be recrystd. The diphenylene methylenecarbonic acid potassium salt, is prepd. analogously. With acetic, isobutyric and succinic acids, no rearrangement could be effected. The fact that from K malonate no enol deriv. has been prepd. may indicate that a connection exists between the strength of the acid and the tendency to enolization. $\text{Ph}_2\text{CHC}(\text{O})\text{OK}$, a weak acid, may exist as such, and also as $\left[\text{Ph}_2\text{CHC} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array} \right] \text{K}^+$, hut $\text{CH}_2(\text{CO}_2\text{K})_2$ exists only as $\left[\text{CH}_2 \begin{array}{c} \diagup \text{CO}_2 \\ \diagdown \end{array} \right] \text{K}^+$. The

similar failure of $(\text{CO}_2\text{H})_2$ to form an enol deriv. may be due to the structure $\left[\begin{array}{c} \text{CO}_2 \\ | \\ \text{CO}_2 \end{array} \right] \text{K}_2^+$.

Methylene carbonates are yellow salts, even more reactive than the ester salts, converted by moisture to the corresponding carboxylates. By the action of air or O_2 on H, an explosive peroxide is formed, which can be isolated as a colorless compd., decomp. under the influence of moisture or heat, to Ph_2CO and K_2CO_3 . Oxidation of H in warm C_2H_4 , yields traces of Ph_2CO , and a monoxide, from which on boiling with alkali or

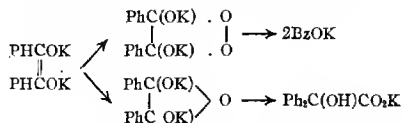
acid, benzoic acid may be obtained. 4.5 g. H in Et₂O, boiled 6 hrs. with 6 g. Me₂SO₄ and pptd. with H₂O, yields Ph₂CMeCO₂Me. Similar treatment with MeI yields after acidification Ph₂CMeCO₂H, m. 170-3°. With AcCl, BzCl, and Ac₂O no reaction occurred. With Ph₂C:CO, F and G could not be isolated. Ph₂C:C(OK)₂ oxidizes spontaneously to fluorenone and CO₂. From *p*-MeC₆H₄CH₂CO₂Ph, a salt can be obtained by the action of KNH₂ which oxidizes spontaneously to Ph(MeC₆H₄)C:CO. The di-K salts of A and its homologs can also be prepd. by adding the corresponding carboxylate to 1 atom K in liquid NH₃. The salts of these enol compds. are much more reactive than the esters. This is comparable with the greater reactivity of the phenolates (cf. preceding abstr.), as compared with the phenols and their esters. The abnormal alkylation of the polyhydric phenols evidences the greater reactivity of the double bond of the ring in the case of these phenolates, as of other enol salts. The deeper color of the enol salts, in comparison with that of their ethers, is similar to the phenomenon as observed in the phenols. These observations, together with the different absorption of the salts and ethers in the ultra-violet bear out Hantzsch's theory of the structure of salts of org. acids.

I. P. ROLF

The alkali henzilates and the henzoic acid rearrangement. H. STAUDINGER AND A. BINKERT. *Helvetica Chim. Acta* 5, 703-10(1922).—The high degree of reactivity attained by the multivalent phenolates is directly connected with the increased unsaturation of the ethylene linkage, caused by the introduction of an *O*-Me group (cf. preceding abstr.). *Potassium stilbenediolate*, [PhC(OK)]₂, (A), was prepd. as an aliphatic ethylene deriv. which is sym. in the same sense as is pyrocatechol or pyrogallol. A, which is the isomer of Ph₂C:C(OK)₂, and the enol deriv. of benzoin (B), can be prepd. (10-20% yield) by the action of KNH₂ on B, or better by adding 1 mol. benzil to 2 mols. of K, and vigorously shaking in boiling C₆H₆ in an atmosphere of anhyd. N. This dark red brown salt, which could not be recrystd., decomps. quant. on addn. of H₂O to benzoin, m. 135°. With Ac₂O it gives colorless *β*-stilbenediol diacetate, which crystals from MeOH and m. 127°. If 1 mol. each of benzil and K be used, or to A, in C₆H₆, an additional mol. of benzil be added, a blue-violet ppt. (C) is formed, which on further addition of K is changed to A. C is not the mono-K salt, but is the *quinhydrone* derivative: PhC(OK) . . . O:CPh

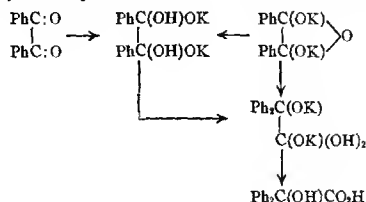
|| | This, with Ac₂O, BzCl, Me₂SO₄ gives 1 mol. A and 1 mol. benzil.
PhC(OK) . . . O:CPh

The strength of coloration of the salts in comparison with the lack of color in the ethers and esters may be compared with the greater absorption in the ultra-violet of the phenolates, especially of pyrocatechol, and may be considered as an index of the greater reactivity of these salts. Oxidized by passing heated dry air over the dry salt, A yields 75% BzOK (cf. preceding abstr.) and 25% Ph₂C(OH)CO₂K. In warm C₆H₆ 50-80% of the latter product is formed. These salts are apparently formed by the decomposition of a peroxide (which could not be isolated), and a monoxide,



These expts. may indicate that in the *benzoic acid rearrangement*, alkali induces a primary rearrangement on benzil, this product being a pinacol deriv. Whether from the latter

primarily an ethylene oxide is formed, which rearranges, or whether the monoxide, formed by oxidation, on the addn. of H goes into the pinacolin type which rearranges, cannot be settled by these expts.



I. P. ROUF

The transformation of methyl α -eleostearate into methyl β -eleostearate. R. S. MORRELL. *J. Soc. Chem. Ind.* 41, 328T (1922).—Bauer and Herberts (*C. A.* 16, 3550) failed to acknowledge M.'s earlier work (*C. A.* 13, 130) on this transformation.

T. S. CARSWELL

Symmetrical diisopropylhydrazine and its derivatives. II. HARRY L. LOCKYER WITH WILLIAM A. NOYES AND JAMES R. BAILEY. *J. Am. Chem. Soc.* 44, 2556-67 (1922); cf. *C. A.* 16, 904.—The *sym*-diisopropylhydrazine (A) described in the 1st paper was not quite pure; a product shown by I titration to be 99.5% pure can be obtained by carefully distg. the product (dried as long as 5 days over Al-Hg) in an inert gas and removing the traces of azo oxidation product by bubbling N through it until n does not change in the course of 15 min. So purified, A b_{760} 124.5°, d_4^{25} 0.7844, n_D^{25} 1.4125. Oxalate, m. 200° after 6 crystns. from alc. Semicarbazide derivative, $C_7H_{17}ON_3$, from KCNO and 1 mol. A.HCl, m. 100°. In the course of attempts to reduce $(N:CMC_2)_2$ by other means than catalytic reduction, BzCl was used in the hope of isolating possible reduction products but the cryst. product immediately obtained in every case was Hoffman and Frey's 1-benzoyl-3,5,5-trimethylpyrazoline (*Monatsh.* 22, 760 (1901)), which is also formed when BzCl is added directly to the ketazine. When 20 g. A.HCl is allowed to stand with a 30% excess of dry CuO in a stoppered flask it gives 19 g. 2,2'-azobispropane (B), $(Me_2CHN:)_2$, faintly straw-colored oil, b_{750} 88.5°, of a nauseatingly sweet and very characteristic odor, neutral to litmus, insol. in dil. acids or alkalies, n_D^{25} 1.3890, d_4^{25} 0.7408, reduced by H and colloidal Pd, Na-Hg or Na and alc. to A, is not appreciably altered by boiling 4 hrs. with 4% HCl but when refluxed 1 hr. with 18% HCl it is hydrolyzed to $Me_2CHNHNH_2$ and Me_2CO . Attempts to isolate the *acelone isopropylhydrazone* (C), which is undoubtedly an intermediate product in the hydrolysis, failed, probably because it instantly hydrolyzes in acid soln., but the C can be obtained in small yield by allowing A to stand 1 week in contact with solid alkali or heating it 3 hrs. at 180° in a sealed tube with solid NaOH or KOH. Isopropylhydrazine is best prepd. by reducing an equimol. mixt. of $N_2H_4 \cdot H_2O$, Me_2CO and HCl with H, H_2PtCl_6 , gum arabic and "seeding colloid." It is very unstable, constantly gives off tiny bubbles of gas even when freshly distd. and kept under N, reduces Fehling soln., $AgNO_3$ and even K_2CrO_4 in the cold, b_{760} 106-7°, yield, 80-90%. Hydrochloride, m. 114°. Benzoylation, even with only 1 mol. BzCl, always gives the *dibenzoyl derivative*, needles from EtOH- H_2O , m. 161.5°. Phenylthiosemicarbazide, fine silky needles, m. 141.5°. C is best prepd. (yield, about 80%) from an equimol. mixt. of anhyd. $Me_2CHNHNH_2$ and Me_2CO in an equal vol. of abs. alc.; it is a mobile liquid of stinging menthol-like odor, b_{760} 132-4°, d_4^{25} 0.8225, n_D^{25} 1.4360, easily reduced catalytically but much more difficultly by Na and alc. to A, completely decompd. by strong and only partially by

weak oxidizing agents (including air). *Nitroso-sym-diisopropylhydrazine*, best prepd. (65% yield) from a paste of 1 mol. each of A.HCl and NaNO_2 with H_2O heated 1 hr. at $60-70^\circ$, has a deep straw color and a peculiar sweetish odor, b_p , $65-6^\circ$, decomps. rapidly $160-2^\circ$ under atm. pressure, is unstable at room temp., gives the Liebermann reaction in the cold, gives with FeCl_3 in H_2O a blue-violet, in alc. a green and in CHCl_3 or C_6H_6 a red color, d_4^{25} 0.9440, n_D^{25} 1.4420, gives with very concd. alc. NaOH or with NaOEt a sodium salt, fine needles. All attempts to reduce the NO group, catalytically or otherwise, failed, the products always being NH_3 , A and unchanged NO compd., with small amts. of unidentified products. Concl. detns. on $\text{Me}_3\text{CHNHNH}_2$ showed that even in a 1:1 soln. it is appreciably hydrolyzed and that in 0.0156 N soln. the hydrolysis is practically complete. For A , using the value Λ_γ for the HCl salt as calcd. according to Bredig $100\gamma/(1-\gamma)v$ of the base is 0.00020, indicating that A is nearly as strong a base as N_3H_4 . C. A. R.

Amino acids. I. The formation of some volatile oils from leucine. SHINTARO KONAMA. *J. Biochem. (Japan)* 1, 213-7(1922).—"It is a remarkable fact already noticed by chemists that a great many non-nitrogenous substances found in living bodies have a close relation with proteins, but none or very few flower essences, fruit oils, and flavors of fermentation products seem to have been actually produced from proteins by pure chem. methods so far as can be gleaned from chem. literature and it has remained as an interesting problem to synthesize such perfumes and to produce them technically from proteins." *Isoamyl isovalerate* is produced by thermal decompn. of anhydroleucic acid from leucine first as the aldehyde and is purified as the bisulfite compd. A good yield of the isovalerate is obtained by treating the aldehyde with $\text{Al}(\text{OAm})_3$. *Ethyl l-acetylleucate*, $\text{l-Me}_2\text{CHCH}_2\text{CH}(\text{OAc})\text{CO}_2\text{Et}$, is prepared by treating *l*-leucic acid from gluten with alc. H_2SO_4 . This gives ethyl *l*-leucate, b_{18-20} $87-9.5^\circ$, which is boiled on the sand bath for 4 hrs. with an equal wt. of AcCl , the product being thrown into H_2O and neutralized with alkali. The oil, which is colorless and of agreeable odor, b , $120-1^\circ$, is extd. with ether. *Methyl l-acetylleucate* is similarly prepd. from *Me l*-leucate with Ac_2O . *Ethyl l-benzoylleucate*, prepd. by heating *l*-leucic acid with BzCl , is a colorless oil which b , $174-6^\circ$ and has a weak turpentine odor. *Ethyl l-isovalerylleucate*, prepd. by heating *Et l*-leucate with isovaleryl chloride, a colorless oil, b , $125-8^\circ$, with a weak peppermint odor. *Amyl l-monochloroisocaproate* prepared by warming *l*-chloroisocaproic chloride with AmOH , is an oil with an odor of overripe oranges, b , $113-4^\circ$. S. MORCULIS

Synthesis of urea from ammonia and carbon dioxide. N. W. KRASE AND V. L. GADDY. *J. Ind. Eng. Chem.* 14, 611-6(1922).—"The first stage in this synthesis consists in the production of $\text{H}_2\text{NCO}_2\text{NH}_4$ from NH_3 , CO_2 and H_2O . This is accomplished by condensing a mixt. of NH_3 and CO_2 , (2:1 by vol.), which carries along with it the requisite amt. of H_2O . The condenser consists of a cylindrical tube surrounded by a jacket, in which the cooling medium circulates, and provided with a rotating, scraping blade fitting inside the tube. The $\text{H}_2\text{NCO}_2\text{NH}_4$ is pressed into briquets and placed in an autoclave heated to 160° . Under the most favorable conditions a conversion into urea of about 40% is obtained. After the heating, the autoclave sludge, now in the liquid form, is run into a still and the unconverted NH_3 and CO_2 distd. off and used in making a fresh charge of carbamate. Cost considerations show that this process has com. possibilities, the chief factor in the com. production being the cost of NH_3 . Historical and theoretical considerations of the reactions are given as well as detailed discussions of expts. with a small exptl. plant. G. W. STRATTON

The urea dearrangement. T. L. DAVIS AND H. W. UNDERWOOD, JR. *J. Am. Chem. Soc.* 44, 2595-604(1922).—"The term 'urea dearrangement' is used to designate the reverse of the reaction $\text{NH}_4\text{CNO} \longrightarrow \text{CO}(\text{NH}_2)_2$. The reaction provides a simple

means of interpreting and correlating a considerable no. of reactions in the urea and guanidine series and of synthesizing certain substituted ureas and thioureas. It is shown in the present paper to occur when urea, thiourea, substituted ureas and thioureas and guanidine are heated. From 93 g. PhNH_2 and 60 g. urea heated 1 hr. at 160° are obtained NH_3 , 19.9% unchanged PhNH_2 and 40.2% $\text{PhNHCONH}_2 + \text{CO}(\text{NHPh})_2$; from 6 g. urea and 20 g. PhNH_2 , 52.3% phenylated ureas; from 6 g. urea and 30 g. PhNH_2 , 81.0% phenylated ureas. The urea dearranges into NH_3 , which escapes, and HNCO , which combines with the PhNH_2 to PhNHCONH_2 ; the latter dearranges at 160° in 2 ways (into $\text{PhNH}_2 + \text{HNCO}$ and into $\text{PhNCO} + \text{NH}_3$) and the PhNH_2 produced in the 1 way combines with the PhNCO formed in the other, giving $\text{CO}(\text{NHPh})_2$. PhNHCONH_2 heated alone gives 77% $\text{CO}(\text{NHPh})_2$. (β - $\text{C}_{10}\text{H}_7\text{NH}_2$), CO , m. 296° (decompn.), is obtained in 45.5% yield from 15 g. β - $\text{C}_{10}\text{H}_7\text{NH}_2$ and 3 g. urea heated 1 hr. at 160° , and the α -isomer, m. 286° , in 75% yield from urea and 3 mols. of the amine heated 3 hrs. (p - $\text{MeC}_6\text{H}_4\text{NH}_2$), CO , m. 284° , is similarly obtained in 53% yield after 2 hrs. and the o -isomer, m. 248° , in 77.5% yield after 7 hrs. *sym*-Disubstituted ureas, in which the substituents are alike, can dearrange in only 1 sense and a sec. amine heated with urea therefore should give only the *unsym*-disubstituted compd. Thus, Ph_2NH and urea heated at 160° , then at 180° , give off NH_3 slowly and yield $\text{Ph}_2\text{NCONH}_2$ but no biuret. PhNHEt apparently does not react with urea; NHBu_2 and NHAm_2 and their HCl salts heated with urea give NH_4Cl but the products are exceedingly difficult to sep. and the aliphatic amines will be the subject of a later investigation. An equimol. mixt. of PhNH_2 and $\text{CS}(\text{NH}_2)_2$ heated 4 hrs. at 160 – 5° and another hr. at 170 – 5° gives H_2S and 12.9% $\text{PhNHCSNH}_2 + \text{CS}(\text{NHPh})_2$, while 1 mol. each of $\text{CS}(\text{NH}_2)_2$ and $\text{PhNH}_2 \cdot \text{HCl}$ after 2.5 hrs. at 160° give 9.7% phenylated thioureas. NH_4NCS (76 g.) and 96 g. PhNH_2 give 20.8% PhNH_2 and 16.8% phenylated thioureas after 2 hrs. at 160° . PhNHCSNH_2 heated alone or with PhNH_2 gives H_2S , PhNCS , NH_3 , PhNH_2 and $\text{CS}(\text{NHPh})_2$. $\text{CS}(\text{NHPh})_2$ dearranges into PhNCS and PhNH_2 , which recombine, and when it is distd., either alone or in a current of HCl , the distillate consists of $\text{CS}(\text{NHPh})_2$, contaminated with PhNCS enough to give a smell but not enough to be isolated. PhOH heated with PhNHCONH_2 or $\text{CO}(\text{NHPh})_2$ gives no PhNHCO_2Ph . Guanidine carbonate heated in a test-tube yields NH_3 and cyanamide, and in a sublimation app. melamine. Cyanamide may be considered as cyanoammonia, NH_2CN , or isocyanamic acid, $\text{HN}:\text{C}:\text{NH}$, and the above reaction can be represented by the scheme $\text{H}_2\text{NC}(:\text{NH})\text{NH}_2 \longrightarrow \text{HN}:\text{C}:\text{NH} + \text{NH}_3$. Since it is a deriv. of both NH_3 and HNCO , it combines with itself as NH_3 does with HNCO , or "polymerizes" to $\text{H}_2\text{NC}(:\text{NH})\text{NHCN}$, which dearranges in 2 ways; on heating it gives NH_3 , melamine (the polymerization product of cyanamide) and mellon (evidently the trimer of NCNHCN or $\text{HN}:\text{C}:\text{NCN}$). When PhNH_2 is heated 5 hrs. at 170 – 80° with guanidine carbonate, 95% of the PhNH_2 is recovered unchanged and a little melamine is formed. $\text{H}_2\text{NC}(:\text{NH})\text{NHCN}$ gives ammeline when heated with urea and thioammeline with $\text{CS}(\text{NH}_2)_2$ or NH_4NCS , the HNCO or HNCS formed by the dearrangement of the urea or thiourea combining with the $\text{H}_2\text{NC}(:\text{NH})\text{NHCN}$ to the ammeline or thioammeline as cyanamide does to form melamine.

C. A. R.

p-Cymene. IV. The chlorination of 2-amino-*p*-cymene. ALVIN S. WHEELER AND I. V. GILES. *J. Am. Chem. Soc.* **44**, 2605–12 (1922); cf. *C. A.* **16**, 1083. — 2-Acetyl-5-chloro-*p*-cymene, obtained in 80% yield from 2,4-AcNH(Me_2CH) $\text{C}_6\text{H}_3\text{Me}$ in CCl_4 with Cl , needles from alc., m. 109 – 11° , hydrolyzed by boiling dil. NaOH to the free amine (A), light red oil with an PhNH_2 -like odor, b. 240 – 50° , heavier than H_2O , and by boiling dil. HCl to the amine hydrochloride, pearly plates, begins to darken 206° , decomps. 228° , slightly hydrolyzed by H_2O ; sulfate, plates from dil. H_2SO_4 , m. 139° , becomes light brown in the air after a few days, seps. from stronger H_2SO_4 in needles,

m. 179°, with only 17.48% SO_4 (apparently owing to H_2O of crystn.). *2-Benzamino derivative* (8 g. from 8 g. A in C_6H_6 heated 4 hrs. with an excess of BzCl), needles from alc., m. 137.5°. *2-Hydroxy compound (5-chlorocarvacrol)* (2 cc. from 10 g. A diazotized in cold dil. H_2SO_4 and then heated on the H_2O bath), viscous liquid, b_p 158°. *2-Methyl-4-chloro-5-isopropylbenzoic acid*, obtained through the nitrile (plates, m. 103°) by the Sandmeyer reaction, silky needles from alc., m. 125°. *2,2'-Diazamino-5,5'-dichloro-p-cymene*, obtained in 80% yield from AlHCl in H_2O at 0° with 0.5 equiv. of NaNO_2 , long yellow needles from ligroin, m. 135-7°. The diazotized A cannot be coupled with amines but couples readily with phenols yielding azo dyes producing on wool and silk colors which are fast to light and washing. In this way were prepd. the *bis-4-[5-carvacrylazo] derivatives of: phenol*, from diazotized A and PhOH , fine yellowish bronze needles from AcOH , m. 196°, sol. in H_2SO_4 with rose-red, in AcOH with dark red color, dyes wool a capucine yellow and silk a Cd yellow; *resorcinol*, bronze-colored needles from ligroin, begins to darken 170°, m. 188° (decompn.), sol. in concd. H_2SO_4 with carmine color, dyes wool a Brazil red and silk a Morocco red; *salicylic acid*, very fine brown micro-needles from ligroin, m. 165°, sol. in H_2SO_4 with scarlet color, dyes wool a Mars-orange color; *1-naphthol*, brown microneedles from alc. or ligroin, m. 128° (decompn.), sol. in AcOH with red, in H_2SO_4 with dark nigrosine-violet color, dyes wool a claret brown; *2-naphthol*, red hexagonal plates from alc., m. 163°, sol. in H_2SO_4 with intense violet color, dyes wool and silk scarlet; *1-naphthol-2-sulfonic acid (sodium salt)*, prismatic plates of burnt-sienna color, sol. in H_2SO_4 with a prune-purple color, acts as a direct dye in the presence of a little AcOH , dyes wool a burnt-sienna and silk an English-red color; *1-naphthol-4-sulfonic acid*, scarlet-red, m. 246° (decompn.), sol. in H_2SO_4 with carmine color, dyes wool and silk a brilliant scarlet; *2-naphthol-7-sulfonic acid*, Nopal-red crystals from alc., m. 228° (decompn.), sol. in H_2SO_4 with pomegranate-purple color, dyes wool scarlet-red and silk scarlet. The N-Ac deriv. of A heated 2 hrs. at 80° with KMnO_4 in a soln. kept neutral with MgSO_4 yields *2-acetamino-4-isopropyl-5-chlorobenzoic acid*, hair-like needles from dil. alc., softens 206.5°, m. 207-9°, hydrolyzed by boiling dil. HCl to the *2-amino acid*, light grayish yellow needles from alc., m. 159°, whose *hydrochloride*, plates from dil. HCl , m. 178°. Diazotized A treated with CuCl and then oxidized by heating 10 hrs. in a sealed tube at 180° with 20 parts HNO_3 (d. 1.15) gives $2,5,1,4\text{-C}_6\text{H}_2\text{Cl}_2(\text{CO}_2\text{H})_2$, m. 305°. C. A. R.

A new depolymerization product of starch. AMÉ PICTET AND R. JAHN. *Helvetica Chim. Acta* 5, 640-5 (1922).—The isolation of a new trihexosan indicates that starch is an aggregate of links composed of 3 hexose groups, rather than a polymer of an anhydride of maltose. By heating potato starch in 10 parts of glycerol at 200-10° until the soln. just fails to give a color with I (about 45 min.) and then quickly removing the solvent by vacuum distn. at the same temp. P. and J. obtain a transparent vitreous, light brown solid. Soln. in H_2O and pptn. with EtOH gives a white, amorphous slightly hygroscopic powder (90% of the original wt.), *trihexosan*, $(\text{C}_6\text{H}_{10}\text{O}_5)_3$ (A), not identical with triamylose (cf. Pringsheim, *C. A.* 8, 118; Karrer, *C. A.* 16, 1746) or isotriamylose, sol. in pyridine, insol. in HOAc and the usual solvents, decomp. without m. 230-2°, mol. wt. 503, $[\alpha]_D^{25}$ 162.2° (H_2O), does not taste sweet, does not reduce Fehling soln., is not pptd. by I-KI soln. Hydrolysis with H_2SO_4 yields glucose (osazone m. 204°). A acetylated with 7 pts. Ac_2O , yields *trihexosan monoacetate* $(\text{C}_6\text{H}_7\text{O}_4\text{Ac})_3$, colorless amorphous powder, from EtOH , sol. in Me_2CO , HOAc , C_6H_6 , pyridine, EtOH and MeOH , insol. in H_2O , Et_2O and petroleic ether, m. 153-4°, decomp. 270°, mol. wt. 871, $[\alpha]_D^{25}$ 125.9° (HOAc). I. P. ROLF

Plant colloids. XIII. Synthetic amylophosphate. M. SAMEC AND ANKA MAYER. *Kolloidchem. Beihefte* 16, 89-98 (1922); cf. *C. A.* 7, 3767; 15, 3983.—Esterifying erythroamylose (B) obtained from starch granules with H_3PO_4 gave a product (C) which

in external appearance corresponded completely to native amylopectin (A). The % of P_2O_5 in the dry substance for A was 0.175; for B 0; for C 2.19. The values for other measurements on A, B and C, resp., were: conds. ($K \times 10^3$) of 2% solns., 8.21, 0.52, 29.21; viscosities of 1% solns. compared with H_2O , 14.96, 1.16, 17.7; mol. wt. 113,000, 158,800, 62,500. If anhydromaltose (cf. Karrer, *C. A.* 15, 2631) be the elementary mol. of the starch substance, the formulas corresponding to these stoichiometrical relations would be, for A, $(C_{12}H_{22}O_{11})_{34}(H_2PO_4)_1$ and for C, $(C_{12}H_{22}O_{11})_{14}(H_2PO_4)_{11}$. Esterifying amyloamyloses with H_2PO_4 also gave a gelatinous substance like amylopectin. The % P_2O_5 in this product was 2.06; the cond. ($K \times 10^3$) of a 2% soln., 91.3; viscosity of 1% soln., 43.1 and mol. wt. 10,300. These results correspond to the formula $(C_{12}H_{22}O_{11})_{30}(H_2PO_4)_1$. Since the colors produced by I with the synthesized product and the initial materials were similar, the coloring power of I within wide limits is independent of the degree of hydration and association. H. M. McLAUGHLIN

The preparation of cyclohexanol. ANDRÉ BROCHET. *Compt. rend.* 175, 583-5 (1922).—A more detailed study of the reduction of PhOH by H with Ni as catalyst is reported (cf. *C. A.* 8, 3180). At atm. pressure PhOH contg. 10% active Ni by wt. absorbed H only slowly up to 50°. The following data gives the temp. and the no. of cc. of H absorbed per g. of Ni per min. (sp. activity) resp.: 55°, 0.55; 65°, 0.72; 78°, 0.83; 87°, 1.39; 95°, 2.22; 113°, 3.33; 123°, 4.11; 145°, 5.55. At 10-15 atm. pressure, the absorption of H was rapid between 100-50°, and the transformation to $C_6H_{11}OH$ was complete. No intermediate product was detected in any expt., even at the beginning of the reaction. The $C_6H_{11}OH$, filtered, washed with dil. NaOH, then with H_2O , and distd., b₇₆₀ 160-1°, m. 23.5°. It is recommended that at least 5 parts of Ni per 100 be used, under which conditions it can be used a great no. of times. Using 40 g. of Ni, 8 hydrogenations of 700-g. portions of PhOH were made with a daily absorption of 450-500 l. of H. The 9th hydrogenation required 3 days, with absorptions of 250, 150 and 50 l. per day. The Ni, washed with EtOH and dried, did not effect further hydrogenation of PhOH, but did hydrogenate PhCH:CHCO₂Na in alk. soln. at atm. pressure at almost its normal rate. C. C. DAVIS

The manufacture of 1,3,5-trinitrobenzene. ALAN A. DRUMMOND. *J. Soc. Chem. Ind.* 41, 338-40 (1922).—By nitrating 20 g. of *m*- $C_6H_4(NO_2)_2$ for 3 hrs. at 130° with 80 g. of 90% HNO_3 and 296 g. of 22% oleum, a yield of 29% of $C_6H_3(NO_2)_3$ was obtained, together with a 24% recovery of the $C_6H_4(NO_2)_2$. With less HNO_3 the total yield of $C_6H_3(NO_2)_3$ is smaller, but the loss by oxidation is less. With more HNO_3 the loss is greater, but the product is nearly free from $C_6H_4(NO_2)_2$. By the nitration of $Cl_3CH_2-(NO_2)_2$ a 68% yield of *picryl chloride* can be obtained. Since the Cl in the latter can be readily split off, $C_6H_3(NO_2)_3$ can be made more economically from $ClC_6H_3(NO_2)_2$ than from $C_6H_4(NO_2)_2$. A f.-p. curve for mixts. of $C_6H_4(NO_2)_2$ and $C_6H_3(NO_2)_3$ is given. T. S. CARSWELL

Preparation of phenylimidophosphgene and the chlorination of formamidine. R. S. BLY, G. A. PERKINS AND W. LEE LEWIS. *J. Am. Chem. Soc.* 44, 2896-903 (1922).—Phenylimidophosphgene (A) was used for a short time by the Germans as a war gas. It is a mild lung irritant, producing nausea, sometimes vomiting, soreness of the throat, tightness in the chest and pains in the stomach, followed by coughing and bronchitis, but lachrymation is not a prominent feature. In experimental animals it produces corneal ulcers, which do not, however, tend to permanent blindness. It is ordinarily prepd. by the chlorination of PhNCS. The PhNCS, b. 215-21°, was obtained in 70% yield, together with 83% PhNH₂, by refluxing 3689 g. H_2SO_4 (2 vols. of 1.84 acid and 5 vols. H_2O) and 1140 g. CS(NHPh)₂ 6 hrs.; satd. in CCl_4 or CS_2 with Cl, it gives 90-7% A, b₇₆₀ 104-6°. By using A itself as the solvent in the chlorination of PhNCS, the CCl_4 or CS_2 can be dispensed with and the product fractionated at once under atm. pressure.

It was thought that formamliide (B) in either of its tautomeric forms might be chlorinated to A. The B, m. 45-7°, b₁₁ 159-62°, was obtained in 88% yield from PhNH₂ and HCO₂H by Tobias' method. With SCl₂ or Cl in the cold, with or without solvents, B in all cases gives 2,4-dichloroformamliide (C), m. 158-9°. On first adding the SCl₂ to the B there is formed a hygroscopic solid, apparently an addn. product. Chlorination in the presence of PCl₃ and POCl₃ gave only mixts., sepd. with difficulty and contg. no A. With SOCl₂ the course of the reaction is profoundly affected by the character of the SOCl₂; the presence of traces of POCl₃, especially, greatly diminishes the amt. of Cl taken up; in this work a product b. 74-6.5° was used. B in 6 parts of a mixt. of equal parts of CHCl₃ and SOCl₂ was satd. with Cl below 10°, 100 g. B requiring on an av. 3 hrs. and taking up about 100 g. Cl. From the product were isolated C, A, *p*-chlorophenyl-imidophosgene, b₁₀ 135-7° (which with PhNH₂ gives the hydrochloride, m. 247-50°, of *p*-chlorotriphenylguanidine, m. 135-6°), and 2,4-dichlorophenylimidophosgene, b₁₀ 150-3° (giving with PhNH₂ the hydrochloride, m. 207-9°, of 2,4-dichlorotriphenylguanidine, m. 129.5-30.5°). C. A. R.

Catalytic preparation of azobenzene and aniline. II. C. O. HENKE AND O. W. BROWN. *J. Phys. Chem.* 26, 631-8(1922).—The reduction of PhNO₂ (A) by H to form azobenzene (B) and PhNH₂ (C) is continued (cf. C. A. 16, 1939) with other catalysts, using almost the same app. With Ti as catalyst, B was formed almost to the exclusion of C, but with small yields of azoxybenzene. With Au, almost theoretical yields of C were obtained, but the activity decreased with use. At 355° the yield of C was 99.7%. Hg had no catalytic activity. The activity of Ti decreased very rapidly with use, probably caused by its melting and running together. A yield of B as high as 90.2% was obtained at 260° with 13% excess of H (calcd. for B). Correlating the yields of B obtained with Hg, Au, Ti, Pb and Bi as catalysts, it is found that *catalytic activity is a function of atomic wt.* C. C. DAVIS

Tetraphenyldiarsine. PARRY BORGSTROM AND MARGARET M. DEWAR. *J. Am. Chem. Soc.* 44, 2915-23(1922); cf. C. A. 14, 183.—The present work was an attempt to det. whether or not Ph₄AsAsPh₄ (A) would dissociate into radicals of the type Ph₂As· capable of independent existence. The A was prepd. as described in the earlier paper and m. 130-0.5°, the m. p. detns. being made in the original app. where there had been no opportunity for absorption of O; Michaelis and Schulte (*Ber.* 15, 1952(1882)) give 135°. Exposed to moist air. A absorbs O with formation of 2Ph₂AsO₂H + Ph₄As₂O, the mixt. softening at 135°, the temp. given by M. and S. as the m. p. of pure A. No peroxide was isolated, although it may have been formed transitorily. Allowed to stand several hrs. in MeI in a N atm. A gives Ph₂Me₂AsI, m. 189°. In C₆H₆ it absorbs I in amts. varying with the age of the soln. (around 90% of the amt. calcd. for the formation of Ph₂AsI immediately after soln., 60-70% after about 10 min. and reaching a const. value of about 39-40% after longer intervals); if 85-90% of the calcd. amt. of I is dissolved in the C₆H₆ before adding the A, the latter will absorb more I, bringing the total up to 90-9%. In C₁₂H₆ after 2 hrs. or more, around 40% I is absorbed. In freezing C₁₂H₆, it shows mol. wts. varying with the age of the soln. from 520 after 10-5 min. to 766 after 303 min. (calcd. 458); when the mol. wt. is 766, the I absorption is 40-50% of the calcd. A dissolves in liquid SO₂ with brilliant yellow color and the cond. of the soln. increases with time from 4.4 mhos×10⁻⁴ immediately after soln. to 97.4 after 17 days; at the end of this time, after evapn. of the SO₂ in N, the I absorption is 77.7% of the calcd. The cond. of fused A increases with the temp. from 2.95 mhos×10⁻⁴ at 130-2° to 886 at 307-8°, at which temp. the A suddenly blackens with deposition of As. These results indicate that the bond between the As atoms of A is easily broken. Bivalent As of the type Ph₂As may be present in soln. transitorily but it is doubtful if it is the stable form. The valence or configuration of the stable form is unknown. C. A. R.

Addition reactions of the phosphorus halides. V. The formation of an unsaturated phosphonic acid. JAMES B. CONANT AND BERNARD B. COYNE. *J. Am. Chem. Soc.* **44**, 2530-6 (1922); cf. C. A. 16, 68.—As shown in earlier papers, hydroxyphosphonic acids (A), $RC(OH)R'PO(OH)_2$, are obtained by treating most aldehydes and ketones with PCl_3 in the presence of glacial AcOH, pouring the mixt. into H_2O and evapg. the soln. to dryness. In the case of certain ketones considerable amts. of an unsatd. phosphonic acid are also formed. In the addn. of PCl_3 to BzH the 1st step seems to be a reversible combination of the 2 substances. In the presence of AcOH or Ac_2O the primary addn. product is transformed into a phosphonic acid; thus, $RCOMe + PCl_3 + AcOH \longrightarrow 2AcCl + HCl + RCMc.O.POOH$ (B). The 1st product sepg. from the $AcCl$ and

excess of AcOH is a gum only slowly transformed into the cryst. A by boiling with H_2O . The similar hydrolysis of the B derived from $PhCOMe$ is complicated by several other reactions: $A + HCl \longrightarrow PhCClMePO_3H_2$ (C) $(-HCl) \longrightarrow PhC(:CH_3)PO_3H_2$ (D). The C is obtained in excellent yield by directly satg. the reaction mixt. with dry HCl; apparently the O ring of the B can be opened by HCl. On hydrolysis in H_2O at room temp. C gives A; the hydrolysis is readily reversible, C being formed from A with concd. HCl. C passes into D on beating either alone or in H_2O ; in the latter case, strangely enough, the reaction is accelerated by the presence of considerable amts. of HCl. Further evidence for the above mechanism of the reaction is furnished by the fact that A heated in pure H_2O does not change but in the presence of HCl is quant. converted into D. The D from $PhCOMe$ readily adds 2 atoms of Br in H_2O or $CHCl_3$ and the resulting di-Br acid (E) loses HBr on beating, forming an unsatd. acid (F), $PhC(:CHBr)PO_3H_2$, while the corresponding satd. acid (G), $PhCH(CH_2Br)PO_3H_2$, is obtained in impure state from D with fuming HBr. E, F and G with aq. Na_2CO_3 lose HBr and H_2PO_4 , forming $PhCBr:CH_2$, $PhC:CH$ and $PhCH:CH_2$, resp. The reaction is far from quant., however; side reactions involving the formation of A reduce the yield of unsatd. compd. H_2O alone converts E into a dihydroxyphosphonic acid (H), $PhC(OH)(CH_2OH)PO_3H_2$. Therefore, when E is treated with aq. alkalis 2 reactions occur simultaneously; that leading to the formation of H seems to be favored by increase in temp. The concn. of HO ions is apparently without much effect within certain limits on the yield of $PhCBr:CH_2$, but when it is very low (about 10^{-12}) little or no cleavage of the mol. takes place and only H is formed. *α-Phenyl-α-chloroethylphosphonic acid* (C) (16 g. from 10 g. $PhCOMe$ and 14.2 g. PCl_3 treated after 2 hrs. with 25 g. AcOH, allowed to stand overnight and treated 20 min. with HCl), long needles from Et_2O , m. $174-5^\circ$; allowed to stand 2 days in H_2O and evapd. at room temp. with a current of air it gives 81% of *α-phenyl-α-hydroxyethylphosphonic acid* (A), m. $154-5^\circ$, does not decolorize Br water, is unchanged by heating in H_2O or C_6H_6 for more than 8 hrs., gives 96% C when satd. in concd. HCl with HCl gas, yields 98% D, m. $112-3^\circ$, when heated above its m. p. D is also obtained in 90% yield from C heated above its m. p. and slowly and incompletely from C boiled in H_2O (17% in 24 hrs., longer boiling producing no further change); in concd. HCl, however, 95% D is obtained after 6 hrs. boiling. A likewise gives 97% D with boiling concd. HCl. D is the main product (88%) when the usual method of prepg. A is applied to $PhCOMe$. *α,β-Dibromo-α-phenylethylphosphonic acid* (E), obtained in 84% yield from D in $CHCl_3$ with Br in CCl_4 , m. $186-8^\circ$, gives with satd. Na_2CO_3 at 0° 68%, at room temp. 16%, with cold concd. NaOH 67-73% $PhCBr:CH_2$, b_m $110-2^\circ$. *α,β-Dihydroxy-α-phenylethylphosphonic acid* (H) (87% from aq. E evapd. on the H_2O bath), m. $143-5^\circ$. *α-Phenyl-β-bromovinylphosphonic acid* (F) (90% from E heated above its m. p. in *vacuo*) m. $133-5^\circ$, does not decolorize Br water but does decolorize $KMnO_4$, gives 37% $PhC:CH$, b. $140-2^\circ$, when allowed to stand a short time in Na_2CO_3 ; 15 g. heated 17 hrs. at 100° in a sealed tube with 100 cc. of 82% HBr gives 15 g. of a product m. $110-40^\circ$, shown to contain

α -phenyl- β -bromophosphonic acid (G) by the fact that with Na_2CO_3 it gives 1% of $\text{PhCH}:\text{CH}_2$. α,β -Dichloro- α -phenylethylphosphonic acid, obtained like E in 83% yield, m. 175-8°.

C. A. R.

Action of thionyl chloride upon substituted benzenesulfonyl chlorides. J. POLAK AND ZOSIA RUDICH. *Monatsh.* 43, 209-24(1922).—This work was undertaken to confirm and extend the work of P. and Schädler (*C. A.* 13, 418). SOCl_2 does not react with $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl}$, even when heated for 24 hrs. When heated in a sealed tube at 140°, a 54% yield of $p\text{-ClC}_6\text{H}_4\text{CHCl}_2$ is obtained, while if the temp. is increased to 240° an almost quant. yield of $p\text{-ClC}_6\text{H}_4\text{COCl}$ is the result. $o\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl}$ does not react with SOCl_2 at 140°, even in a sealed tube, but at 240° about 40% of $o\text{-ClC}_6\text{H}_4\text{-COCl}$ is formed. From these results it might be argued that PhMe should give BzCl , but such is not the case, PhCCl_2 being the only product found. $o\text{-MeC}_6\text{H}_4(\text{SO}_2\text{Cl})_2$ does not react at 170° with SOCl_2 , gives a product which could not be purified at 200° but at 250° gives a compound, $\text{C}_8\text{H}_5\text{Cl}_3$, needles from AcOH , m. 78°. This may be 1,2,4,6-(ClCH_2) $_2\text{C}_6\text{H}_2\text{Cl}_2$ or 1,2-(ClCH_2) $_2\text{C}_6\text{Cl}_4$. An intermediate S-contg. product was isolated, b_p 205-20°, which on further treatment with SOCl_2 gave the compd. m. 78°. At 320°, SOCl_2 gives a product, crystg. in long needles, and m. 193-6°. The action of SOCl_2 upon $m\text{-MeC}_6\text{H}_4(\text{SO}_2\text{Cl})_2$ at 240° gave 4,6-dichloroisophthalyl chloride (*J. prakt. Chem.* 41, 558), m. 75.5-6.5°, as observed by Schädler. Repetition of S.'s expts. at 180° gave no reaction product. If the temp. is raised to 260°, a compound $\text{C}_8\text{H}_5\text{Cl}_3$, long needles, m. 113-4°, is obtained, while at 315-320°, still higher chlorinated products are formed. $p\text{-MeOC}_6\text{H}_4\text{SO}_2\text{Cl}$ and SOCl_2 at 250° gave a pentachlorophenyl chloromethyl ether, needles, m. 211-3°. Its constitution was established by sapon. to $\text{Cl}_5\text{C}_6\text{OH}$.

C. J. WUST

Constitution of resorcinol and some of its derivatives. RENÉ FABRE. *Ann. chim.* 13, 49-116(1922).—The ethylation of resorcinol (A) (Herzig and Zeisel, *Monatsh.* 2, 298(1881)) was slightly improved by using NaOMe instead of NaOH and alc. 4-Chlororesorcinol (B), treated in the same way, gave 1,3-diethoxy-4-chlorobenzene, b_p 145-9°, prismatic needles from alc., m. 32.5° (an -OEt detn., 81% of theory, is held to indicate the presence of 1-keto-2-ethyl-3-ethoxy-4-chloro-1,2-dihydrobenzene); also 1-keto-2,2-diethyl-3-ethoxy-4-chloro-1,2-dihydrobenzene (C), b_p 153-7°, needles, very sol. in most org. solvents, m. 25°. B was also made, but not in solid form, from triethylresorcinol (D) and SO_2Cl_2 in dry Et_2O . $\text{NH}_2\text{NHCONH}_2$ does not give derivs. with A, or with any of its ethylation products. With NaOEt and AmONO at 0°, A gave dinitrosorresorcinol, yellow-brown crystals with $2\text{H}_2\text{O}$ from 50% alc., which lose H_2O at 105°, and then decomp. 115°; also made from mononitrosorresorcinol. B gave nitroso-4-chlororesorcinol, yellow leaflets, sol. in dil. alc., AcOH , and C_6H_6 . NaOMe and A in alc., dried in H_2 in vacuum, and treated with CO_2 under 6 atms., gave 2,4-(HO) $_2\text{C}_6\text{H}_2\text{-CO}_2\text{H}$ (E), and also 4% of the 2,6-(HO) $_2$ deriv. With SO_2Cl_2 in dry Et_2O , E gave 2,4-dihydroxy-3-chlorobenzoic acid (3H₂O), m. (dry) 203°; Na salt (H₂O). B heated with KHCO_3 gave 76% of 2,6-dihydroxy-3-chlorobenzoic acid (3H₂O), m. (dry) 215-6°. E, allowed to stand 24 hrs. in glacial AcOH with xanthylol (F), gave xanthyl-2,4-dihydroxybenzoic acid, softens without m. 200°; sodium salt (2H₂O). Condensation of BzH with A by NaOMe gave an amorphous yellow substance (G); heated on the water bath for 6 hrs., G gave a cryst. product (H), very slightly sol. in hot alc. or AcOH , more so in hot PhCH_2OH , resinifies 100°. BzH and A, heated 6-8 hrs. on the water bath in AcOH , also gave H, benzalresorcinol. (All aldehyde condensation products of A are more probably derivs. of α,β -diphenyl- α,β -di[(dihydroxyphenyl)ethylene]. With Ac_2O and NaOAc , H gave a diacetyl derivative, m. 364-6°, having double mol. wt. Similarly, vanillin gives 3-methoxy-4-hydroxybenzalresorcinol, crystals from PhCH_2OH , has no m. p.; triacetyl derivative, m. 323°; piperonal gives 3,4-methylenedioxybenzal-

resorcinol; diacetyl derivative, m. above 370° ; mol. wt. double in PhNO_2 . **F**, condensed with **A** by NaOMe , gave a resin; but **F** and **A** in AcOH (24 hrs. at room temp.) deposit crystals from which are sepd. xanthylresorcinol (**J**), m. $178-9^{\circ}$; diacetyl derivative, m. $242-3^{\circ}$; and dixanthylresorcinol, m. $255-7^{\circ}$; diacetyl derivative, m. $282-3^{\circ}$. Similarly, xanthyltriethylresorcinol, m. $201-2^{\circ}$; (**F** does not react with tetraethylresorcinol); 2-xanthyl-4-nitrosoresorcinol (**K**), from 4-nitrosoresorcinol, dark red crystals from alc., m. 212 ; 2-xanthyl-4-chlororesorcinol, m. 215° . **J**, with AmONO and NaOMe , gave an isomer of **K**, formulated as 2-nitroso-4-xanthylresorcinol, golden hexagonal leaflets, m. $295-6^{\circ}$. As for **J**, **F** and $p\text{-C}_6\text{H}_4(\text{OH})_2$ gave 2-xanthylhydroquinol, m. $215-6^{\circ}$, and dixanthylhydroquinol, m. $231-2^{\circ}$. Xanthyl-2-chlorohydroquinol, m. $236-7^{\circ}$; xanthylpyrochatechol, m. $235-6^{\circ}$; xanthyl-4-chloropyrochatechol, m. 224° ; 4,5-dichloropyrochatechol does not condense with **F**. [Several of the formulas assigned by **F** are not based on any real evidence, and some are almost surely wrong. ABSTR.] B. H. N.

Influence of substituents in the components on the equilibrium in binary solutions. XXXVII. The systems of *p*-quinone with phenols, amines and hydrocarbons. ROBERT KREMMANN, SEPP SUTTER, FRANZ SITTE, HUBERT STRZELBA AND ALADAR DOBOTZKY. *Monatsh.* 43, 209-313(1922); cf. *C. A.* 16, 560.—In the systems with phenols, the existence of the following compds. was established from the quasi-binary T , x diagrams: 1 quinone (**A**)-2 PhOH , 1A-1 hydroquinol, 2A-1 pyrochatechol, 2A-1 resorcinol, 3A-1 pyrogallol, 1A-1 $\alpha\text{-C}_6\text{H}_4\text{OH}$, 2A-1 $\alpha\text{-C}_6\text{H}_4\text{OH}$, 1 $\beta\text{-C}_6\text{H}_4\text{OH}$ -2A. Only $p\text{-O}_2\text{NC}_6\text{H}_4\text{OH}$ gave a compd. with **A**, in the ratio of 1:1. No evidence of a compd. of **A** and PhCOH was discovered. $p\text{-MeC}_6\text{H}_4\text{NH}_2$ formed an equimol. compd. with **A**, while $\beta\text{-C}_6\text{H}_4\text{NH}_2$ gave compds. with 1 and 2 mols. **A**. **A** does not give solid compds. with Ph_2CH , C_{10}H_8 , acenaphthene, phenanthrene, fluorene, nor with Ph_2NH or carbazole. Exptl. results are given as tables and curves. C. J. WEST

Preparation of benzyl esters of some high-boiling acids. T. J. THOMPSON AND GERALD J. LEUCK. *J. Am. Chem. Soc.* 44, 2894-6(1922).—The esters were prepd. by heating an equimol. mixt. of pure PhCH_2OH and the acid in a 150 cc. flask under a 1-cm. air condenser of suitable length to such a temp. that the vapors of the alc. and acid reached its top but did not escape, while the H_2O formed did. Below are given, resp., the length of the condenser in cm., the length of heating in hrs. and the % yield of ester: succinate, 25, 0.25, 90-5; maleate and fumarate, 25, 0.25, 75; henzoate, 90, 6, 85; phthalate, 50, 5, 60; butyrate, 90, 5, 85; valerate, 90, 8, 85; caproate, 90, 5, 88; caprylate, 50, 4, 80. In the case of the phthalate, the condenser had to be surrounded with steam and the pressure within the condenser tube kept 200 mm. below atm. pressure, and in that of the butyrate 1200 mm. pressure had to be used before reaction took place. C. A. R.

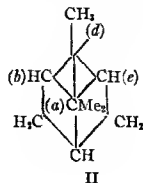
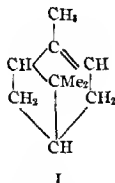
Optically active dyes. I. A. W. INGERSOLL WITH ROGER ADAMS. *J. Am. Chem. Soc.* 44, 2930-7(1922).—An excellent method which should throw light upon the question whether dyeing is a phys. or chem. process is the study of the action of optically active dyes upon fibers; if the absorption by the fibers is a purely phys. process, each of a pair of mirror images would be expected to have the same dyeing properties, while, on the other hand, if a chem. reaction of any kind takes place, a different degree or rate of absorption of the *d*- and *l*-forms might take place on account of the optical activity of the substances of which the fibers are composed. The best method of approach for the prepn. of numerous pairs of optically active dyes in the least time and with a minimum amt. of experimentation consists in seeking known pairs of *d*- and *l*-compds. where the *dl*-forms are readily obtained, where the methods of resolution have been thoroughly worked out and in which certain groups exist that will allow of the conversion of the substances into dyes by one or more easy steps. No other class of compds. fulfills these conditions as satisfactorily as the NH_2 acids or esters, especially $\text{PhCH}(\text{NH}_2)\text{CO}_2\text{H}$ (**A**).

Two pairs of dyes (from β -C₁₀H₇OH and PhNMe₂) have thus far been prepd. and preliminary dyeing tests have been made by treating equiv. solns. of the *d*- and *l*-forms under like conditions with the same amt. of wool and detg. colorimetrically at various time intervals how much of the dye had been absorbed. While the 2 forms of the C₁₀H₇OH dyes are absorbed in the same relative amts. over short as well as long periods of time, one of the 2 forms of the PhNMe₂ dyes is absorbed more rapidly than the other. The *l*-A showed $[\alpha]_D^{25} -157.5^\circ$ (HCl), the *d*-A 153.9°. *dl*-Phenyl-*p*-nitrobenzoylaminoacetic acid (B), obtained in 70-5% yield from A and O₂NC₆H₄COCl in NaOH-NaHCO₃ below 20°, pale yellow needles from 95% alc., m. 184°; *ethyl ester*, pale yellow needles from alc., m. 140°. *p*-Aminobenzoylamino acid (C) (12-4 g. from 20 g. B with NH₄OH-FeSO₄), m. 152°; *hydrochloride*, needles from 1:1 HCl, m. 190-200° (decompn.) on slow, 215° on rapid heating. *l*-Form of B, from *l*-B, yellow needles from AcOEt, m. 163°, $[\alpha]_D^{20} -86.56^\circ$ (abs. alc.) (yield, 90%); *ethyl ester*, yellowish needles from alc., m. 155°, $[\alpha]_D^{20} -67.7^\circ$ (AcOEt); *p*-aminobenzoylamino acid (yield, 65-70%), needles from H₂O, m. 168-9°, $[\alpha]_D^{20} -93.75^\circ$ (N HCl); *hydrochloride*, decomp. 220-2° when plunged into a bath at this temp. *d*-Form of B, m. 163°, $[\alpha]_D^{20} 86.13^\circ$ (abs. alc.); *ethyl ester*, m. 158°, $[\alpha]_D^{20} 67.4^\circ$ (AcOEt); *p*-aminobenzoylamino acid, m. 168-9°, $[\alpha]_D^{20} 93.63^\circ$ (N HCl); *hydrochloride*, needles, m. 220° (decompn.). The compound *dl*- β -HOC₁₀H₆N₂C₆H₄CONHCHPhCO₂H (D), from diazotized B coupled with β -C₁₀H₇OH (yield, practically quant.), orange-red needles from AcOH, m. 252°, readily sol. in alkalies and NH₄OH; *l*-form, orange-red crystals, m. 238°, $[\alpha]_D^{20} -27.25^\circ$ (NaOH) for sunlight; *d*-form, m. 238°, $[\alpha]_D^{20} 28.50^\circ$. *Dimethylaniline* analog of *l*-D, red-brown needles from 50% alc., m. 189-90°; *d*-form, m. 188-9°; no readings of the rotations in abs. alc. in sunlight could be obtained.

C. A. R.

Position of the double linkage in piperitone. II. A. R. PENFOLD. *Perfumery Essent. Oil Record* 13, 322-3 (1922); cf. C. A. 16, 715.—The evidence submitted in the earlier paper showed piperitone to possess the structure of a Δ^1 -3-menthene, a conclusion strengthened by results obtained in the oxidation of piperitone (from *Eucalyptus dives*) with KMnO₄, whereby the following acids were isolated: α -hydroxy- α -methyl- α' -isopropyladipic, m. 143.5°, α -isopropyl- γ -acetylbutyric, b₁₂ 175-7°, and α -isopropylglutaric, m. 94-5°. Also in *J. Proc. Roy. Soc. N. S. Wales* 56, 39-43 (1922). W. O. E.

Formulas of bicyclic terpenes. GEORGES DUPONT. *Bull. soc. chim.* 31, 897-909 (1922).—Theoretical. It is admitted that the current formulas agree with the mol. refraction and with the results of KMnO₄ oxidation. Most other reactions are considered "abnormal." Pinene, nopinene, camphene, fenchene I, fenchene II, and sabinene, are considered. In all, the double bond is held to be more or less "conjugated" with the "bridge" bond. In the case of pinene (I), it is held (the same arguments being



used for the other types discussed) that the reactions are best explained by a system of free valences, or oscillating double bonds (the Kekulé and Baeyer structures for PhH are mentioned). The formula II for pinene illustrates this; addn. can take place at any 2 of the carbons *a, b, d, e*; addition to *b, e*, is the only type not represented by known reactions.

BERN. H. NICOLET

Bromonitrocamphane. P. M. GINNINGS WITH W. A. NOYES. *J. Am. Chem. Soc.* **44**, 2567-73(1922); cf. Forster, *Proc. Chem. Soc.* **28**, 313(1912), and earlier papers.—In connection with the bromonitrocamphane (A), obtained by the action of KBrO on camphor oxime, it yet remained to oxidize the A and identify the oxidation products, and also to prove that bromonitrocamphane anhydride (B) contains a C:O group. By using a larger amt. of Br than recommended by F. in the prepn. of A, *vis.* 600 g. Br, 600 g. KOH and 100 g. camphor oxime, A is obtained almost pure with very little of the green by-product. Refluxed a week with a mixt. of 2 vols. H₂O and 3 vols. concd. HNO₃ it gives camphoronic and camphoric acids; if the oxidation is not so protracted considerable camphor can be isolated. Believing that possibly an intermediate bromonitroso compd. might be formed, with an appreciable lag in the reaction, in the prepn. of A, known amts. of camphor oxime, Br and KOH were caused to react and aliquot portions titrated iodometrically at definite time intervals to det. the amt. of Br used; no definite break in the curve of Br utilization was found. The green product formed during the synthesis of A is not, as F. thought, a hydrate of A but a hydroxynitroso-camphane, the product of a side reaction. F.'s B can be obtained almost quant. by slowly dropping A in petr. ether into a mixt. of concd. H₂SO₄ at -10°; with MeMgI it gives a compound (C), C₁₁H₁₅ONBr, plates, m. 117-8°, insol. in acids and alkalis and yielding by the Schotten-Baumann method a *benzoyl derivative*, m. 113-4°. Boiled a few min. with aq. alc. NaOH, C loses Br and gives NH₃ and an acid of the same m. p. as acetocamphenylcarboxylic acid. These results confirm F.'s formula for B and supplement his data for the isomeric enol form. C. A. R.

Some condensation reactions with *p,p'*-bis(dimethylamino)benzohydrol (Michler's hydrol). MARSTON T. BOGERT AND A. RUDERMAN. *J. Am. Chem. Soc.* **44**, 2612-21(1922).—*Succinylleucauramine* (A), (CH₃)₂CO₂NCHR₂ (R = *p*-Me₂NCH₂H₄), nearly colorless needles from alc., is obtained in about 50% yield from succinimide gently boiled 10 hrs. in alc. with 1 mol. Michler's hydrol (B), yields with HNO₃ about 90% of a *dinitro derivative*, yellowish brown powder from alc., m. 94-6° (decompn.), and with 10% KOH at 100° *p,p'*-bis(dimethylamino)benzohydrolsuccinimidic acid, needles from dil. alc., m. 170°, gradually assumes a pale slaty color on standing. *Phthalyleucauramine* (C), from C₆H₄(CO)₂NH and B in alc. (yield, 80%), greenish yellow prisms or leaflets, m. 186.7°. When concd. H₂SO₄ is used instead of alc. as solvent for the C₆H₄(CO)₂NH and B and the soln. is warmed several hrs. at 100°, alkalies ppt. a colorless *labile isomer* of C (yield, 18-20%), changes into the stable form on long standing in alc. or, slowly, when the dry substance is left in the air; heat accelerates the change. The labile form m. about 90°, changing into the colored form, and gives in concd. or even in dil. H₂SO₄ a colorless or only faintly colored soln. from which on rapid addn. of alkali there seps. a colorless oil congealing to a yellow solid. *Phthalyleucauraminecarbinol*, from C in dil. HCl + AcOH with PbO₂ (yield, 60%), m. 176°. *Dinitrophthalyleucauramine*, from C in dil. HCl with 4 mols. NaNO₂ (yield, 90%), yellowish brown solid from alc. or AcOH, m. 104° (decompn.), does not give the Liebermann reaction. *p,p'*-Bis(dimethylamino)benzohydrylphthalimidic acid, from C and 10% KOH at 100° (yield, 90%), needles from alc., m. 163.8° (decompn.), hydrolyzed by dil. HCl at 100° into phthalic acid and leucauramine, and oxidized by PbO₂ in dil. HCl-AcOH to the *carbinol*, R₂C(OH)NHCOC₆H₄CO₂H, brownish solid from ¹/₂ dil. Me₂CO, m. 187° (yield, 75%). Phthalimidine does not condense with B even after beating 1 day at 100° in alc. with a few drops of AcOH. *Di[bis(dimethylamino)benzohydryl]-phthalide*, from phthalide and 1 or 2 mols. B with a few drops AcOH heated 6-8 hrs. at 100°, reddish brown prismatic crystals from gasoline-xylene (1:2), m. 201°, turned pink by acids and decolorized by alkalis. When 4-nitrophthalimide and B are boiled 10 hrs. in alc. the soln. turns blue but no condensation occurs. *3-Leucauraminyl-*

phthalyleucosuramine, $R_2CHNHC_6H_4(CO)_2NCHR_2$ (3 g. from 0.87 g. 3-aminophthalimide and 3 g. B boiled 10 hrs. in alc. with a few drops AcOH), greenish yellow plates from Me_2CO , m. 219–20°. Saccharin and B do not condense when boiled in equimol. proportions in alc. with or without AcOH, but when the 2 substances are brought together, even in very dil. soln., a deep blue color is produced, presumably owing to the formation of a quinonoid salt of B; the reaction appears to be a delicate test for either compd. SO_2 discharges the color. Anthraquinone, alizarin, α - and β -aminoanthraquinone, thiourea and benzoyleurea do not condense with B in alc. or H_2SO_4 . *p,p'*-

Bis(dimethylamino)benzohydryldehydrothio-p-toluidine, $Me_2CH_2 \begin{array}{c} \diagup S \diagdown \\ \diagdown N \diagup \end{array} CC_6H_4NHCHR_2$,

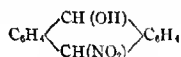
from dehydrothio-*p*-toluidine and B in boiling alc. (yield, 75%), pale yellow microcrystals from C_6H_6 , m. 190–1°. C. A. R.

Certain triphenylmethane dyes. WALTER A. JACOBS AND MICHAEL HEIDELBERGER. *J. Am. Chem. Soc.* 44, 2626–8(1922).—The prepn. in pure state of a no. of dyes of the malachite green series was undertaken as a part of the study of the bactericidal action of dyes in general. The work was discontinued while still incomplete but the chem. results which had been obtained are reported briefly in tabular form. Some of the substances are new. *Leucomalachite green derivatives*: *m*-Acetamino, faintly greenish rhombs from 85% alc., m. 154.5–5.5°; *m*-uramino, needles from alc., m. 194–6°; *p*-diethylamino, cream-colored needles from C_6H_6 -EtOH, m. 142–4.5°; *o*-chloro-*p*-dimethylamino, flat tan needles from PhMe-ligroin, m. 170–1.5°; *p*-hydroxy-5-phenylazo, lenticular platelets from C_6H_6 , m. 186–7°; 2-hydroxy-5-*p*-methoxyphenylazo, ochreous prisms from C_6H_6 , m. 187–8°. *Malachite green derivatives* (the temps. are the decompn. ps. of the anhyd. salts; after the data for the salts are given, in parentheses, the cryst. form of the carbinol and the color it gives with coned. H_2SO_4): unsubstituted malachite green nitrate, olive platelets with H_2O , 130–5° (minute crystals, orange); *p*-methyl chloride, blue-green leaflets with $4H_2O$, 160° (needles, orange); *o*-chloro chloride, voluminous threads, intumesces 170° (octahedrons, orange); *p*-chloro nitrate, green hairs with golden luster, with 3.5 H_2O , 120–75° (minute crystals bright orange); *p*-nitro chloride, purple needles with 5.5 H_2O , 150–5° (minute platelets bright orange); *p*-acetylmethylamino nitrate, green needles with metallic luster, with 0.5–1.0 H_2O , 193–6° (prisms, orange); *o*-chloro-*p*-diethylamino chloride, olive needles with 3.5 H_2O , 185–90° (rhombs, bright orange); *m*-uramino nitrate, olive-green needles with 4 H_2O , 185° (thin platelets, bright orange); *o*-hydroxy chloride, bronze-diamond platelets, 195° (rhombs, dull greenish blue); *p*-hydroxy chloride, hairs, 185–90° (reddish needles, yellowish orange); *o*-methoxy nitrate, bronze needles (leaflets, olive-brown); *m*-methoxy carbinol, beveled hexagonal plates, 147–9.5°, gives with H_2SO_4 a brown color with olive reflex; *p*-methoxy chloride, blue leaflets, 125–40° (needles, orange) *o*-ethoxy carbinol, needles, 178–80°, gives with H_2SO_4 a blue color; *p*-ethoxy chloride, needles and leaflets, 150° (rhombs, orange); 3,4-methylenedioxy chloride, bronze hairs with 4 H_2O , 155–60° (microcrystals, wine-red); *o*-hydroxyacetic acid ether anhydride, grass-green platelets, 170–5°, gives in H_2SO_4 a wine-red color with olive reflex; iuro nitrate, olive-green hairs with bronze luster, with 5 H_2O , 190° (the carbinol gives a brown-purple color with H_2SO_4); brilliant green nitrate, brassy aggregates with H_2O , 140–210° (the carbinol gives an orange-brown color with H_2SO_4). C. A. R.

The composition of erythrosin. M. GOMBERG AND D. L. TABERN. *J. Ind. Eng. Chem.* 14, 1115–7(1922).—Evidence is offered to prove that the true compn. of erythrosin (E) is not that adopted by the U. S. Bur. of Chem. but is $C_{30}H_{20}O_{14}Na_2H_2O$. Prepd. by modifying the method of Mühlhauser (cf. *Dingler's Polytech. J.* 263, 99(1886); 283, 258(1892)), it was free from occluded and adsorbed I, but could not be sepd. from approx. 6% of the di-I compd. By converting it into the diacetate and sapon., it

could be purified. One mol. of E combined with 4 mols. of H₂O from H₂O soln. and with 2 mols. of EtOH from EtOH soln. From EtOH contg. H₂O, each solvent was combined. Drying as high as 170° failed to remove all H₂O, and it was impossible to remove it without decomn. Based upon the data gathered, it is suggested that specifications for purity be based upon the following principles: (1) E should be dried to approx. const. wt. at 120–5° and should then, after soln. in very dil. NH₄OH and pptn. with hot HOAc and a little H₂SO₄, give $93.5 \pm 0.5\%$ of its wt. of dry E acid after adding a 0.4% correction for each 100 cc. H₂O per 1 g. sample and (2) the pptd. E acid should give up no I to EtOH and should contain approx. 60.75% I when dry. C. C. DAVIS

Nitration of hydrocarbons in a basic or neutral medium. M. BATTEGAY ANN PH. BRANDT. *Bull. soc. chim.* 31, 910–5(1922).—Anthracene may be nitrated by treatment at 125° with pyridinium nitrate (prepd. by adding HNO₃ to pyridine). The yield of *meso*-mononitroanthracene is about 70%. The mechanism of the reaction is believed to be first the formation of an intermediate dihydronitroanthranol which



loses water and gives rise to the nitroanthracene. When C₁₀H₈ is treated in the same manner, it proves much more resistant to nitration, giving only a 40% yield of α -C₁₀H₇NO₂, and, as a by-product, nitrophthalic acid. J. B. BROWN

Anthraquinone. M. BATTEGAY. *Rev. gén. sci.* 33, 502–17(1922).—A general review of the isomeric anthraquinones dealing especially with the chem. properties of γ -anthraquinone (A) and its action as a chromogen as illustrated by a few A dyes. Numerous references and some unpublished work of B.'s are included. A comparison of *p*-benzo-, α -naphtho-, and γ -anthraquinones shows a gradual change of properties due to an increase in stability with the disappearance of the ethylene linking of the benzoquinone. Their absorption spectra with ultra-violet light are similar and differ widely from that of hexamethylenediketone (curves given), further substantiating the quinonoid structure. A acts as a H carrier in the reduction of certain azo dyes, anthrahydroquinol being the intermediate product. The unsuccessful attempts to employ sol. sulfonates of A in this catalysis were shown, in the case of the β -sulfonate, to be due to the reaction proceeding too far with the formation of anthranol and anthrone derivs. The α -sulfonate of A is only slightly hydrolyzed by H₂SO₄. H easily replaces the SO₃H group when its aq. soln. is treated with Na-Hg and acidified. The β -sulfonate, however, gives largely anthracene- β -sulfonic acid. Anthracene sulfonated with anhyd. pyridine NH₄ sulfate at 125–175° gave only anthracene- α -sulfonate. The SO₃H group is not mobile as in C₁₀H₇. The fact that the main absorption band of A ($\lambda = 3550 \text{ \AA}$) with ultraviolet light is on the edge of the visible spectrum makes it a very sensitive chromogen. The effect of an auxochrome in the α -position is especially marked. The group —NHBz affects the color only when in the α -position (Algol Yellow G). When two auxochromes are substituted, the max. effect occurs when the groups are in the α -positions and especially when in the same ring, *i. e.*, para. The group —NHBz affects the color notably in 1:5 (Algol Yellow R) and in 1:4 (Algol Yellow 5G). The position, however, has no effect on the affinity of the dye for the fabric. A study of the substituted ureas shows that the α, α' -dianthraquinonylfurea would be more highly colored than the β, β' -compd. (Helindon Yellow 3GN), but would not stand the reduction for vat dyeing. The α, β' -compd. is stable and resembles the β, β' -product. The α - and β -monobenzyldiazinoanthraquinones are highly colored, the former orange, the latter yellow. Both are poor vat dyes for cotton, but good for wool. ALVIN C. PURDY

Picolinoylaminooanthraquinones. F. DE BARRY BARNETT. *Chem. News* 125, 143–4(1922).—To the picolinoyl chloride, obtained by boiling for 2.5 hrs. 5.3 g. picolinic

acid and 20 g. SOCl_2 , 5 g. α -aminoanthraquinone in 100 cc. $\text{C}_6\text{H}_5\text{Cl}$ is added and the mixt. boiled under reflux for 1 hr. After filtering the hot soln. to remove resinous matter and adding an equal vol. of alc. α -picolinoylaminoanthraquinone seps., deep yellow crystals from pyridine, m. (decompn.) $282-4^\circ$. On alk. reduction it forms a red vat. β -Picolinoylaminoanthraquinone, almost colorless, m. $257-8^\circ$, is prepd. in a similar way. After drying in a vacuum desiccator it takes up an elec. charge so easily that it was found necessary to make the powder into tablets before weighing for analysis. This difference in color between the α - and β -comps. is common to all acylaminoanthraquinones; only the α -comps. have tinctorial properties which are of any value. The α -compd. was prepd. to find out if the introduction of a strongly basic group into the mol. would lead to the formation of water-sol. derivs. capable of dyeing on a tannin mordant. This was found not to be the case. G. W. STRATTON

Hydrogenated polycyclic compounds. WALTHER SCHRAUTH. *Z. angew. Chem.* 35, 617-8(1922).—A hydrogenated phenanthrene may be synthesized by coupling cyclohexane in the presence of a condensing agent with phenol, sepg. the *o*-cyclohexylphenol, hydrogenating the latter to *o*-cyclohexylcyclohexanol, and again condensing with phenol. The resulting ketone is treated with a dehydrating agent, when a decahydrotriphenylene is formed, which on hydrogenation gives a hydrogenated benzophenanthrene. In a similar manner, substituted phenols give substituted comps. of the same type. With alkylated N comps. new heterocyclic rings may be formed. This synthesis offers a possible explanation of the origin of these comps. in coal-tar.

T. S. CARSWELL

The properties and composition of decalin. J. B. COLEMAN AND P. BULHAM. *Chem. Age (London)* 7, 534-5(1922).—Decalin, used in Germany as a turpentine substitute, consists of 80 vols. of decahydronaphthalene mixed with 20 vols. of tetrahydronaphthalene. Its phys. properties are: d_{15}^{20} 0.8947, n_D^{20} 1.4815, flash-point 51.6° , viscosity at 40° 0.00675, residue on evapn. 0.001935%.

T. S. CARSWELL

Pyrroles and hydroxypyrroles. HANS FISCHER AND MARIANNE HERMANN. *Z. physiol. Chem.* 122, 1-25(1922).—In connection with work on bilirubin derivs. the following derivs. of 2-hydroxy-4-carbethoxy-5-methylpyrrole (A), 2-hydroxy-3,5-dimethyl-4-carbethoxypyrrole (B) and 3-hydroxy-4-carbethoxy-5-methylpyrrole (C) were prepd. A and B were prepd. by the method of Emery (*Ann.* 260, 137(1890)). Diethyl methylacetylsuccinate, used in the prepn. of B, was transformed into the hydrazone by warming 0.2 g. of the ester in Et_2O with 0.11 g. PhNHNH_2 on a H_2O bath for a short time and then cooling. On kneading with petroleum ether the mass solidifies; oily impurities are removed by washing with petroleum ether after which the compd. is crystd. from the same solvent. It m. 85° , is sol. in alc., Et_2O , CHCl_3 , EtOAc , C_6H_6 , Me_2CO , pyridine, AcOH , less sol. in petroleum ether, insol. in H_2O , decomp. on standing. C was prepd. by converting Et acetylsuccinate into Et aminoacetylsuccinate, splitting off EtOH by heating to 150° , and crystg. from H_2O ; yield 20-25%. Diacetyl-2-hydroxy-4-carbethoxy-5-methyl pyrrole (D) results from the action of Ac_2O and a trace of H_2SO_4 upon A; needles from AcOEt , m. 220° (decompn.). Diacetyl-2-hydroxy-3,5-dimethyl-4-carbethoxypyrrole (E), prepd. similarly from B, crystals from CHCl_3 -petroleum ether, sol. in alc., EtOAc , C_6H_6 , Et_2O , MeOH , AcOH , less sol. in CHCl_3 , H_2O and petroleum ether, m. 118° . B heated 24 hrs. on a H_2O bath with 1:2 HI in AcOH is decompd. with the complete liberation of N as NH_3 . 3-Amino-2-hydroxy-4-carbethoxy-5-methylpyrrole (F) (by adding NaNO_2 to 0.85 g. of A in AcOH with cooling in the course of a day, decomp. with 3 g. Zn dust, heating 0.5 hr. on a H_2O bath and filtering, whereupon crystn. occurs), m. 244° (decompn.) when crystd. from alc., sol. in AcOH and HCl but not reprecipd. with alkali, gives a blue color with $\text{MeNC}_6\text{H}_4\text{CHO}$ in HCl . C when warmed with BzH and a bit of KHSO_4 gave yellow needles from alc. m. 228° , of 2-

benzal-3-hydroxy-4-carbethoxy-5-methylpyrrole (G) or its enol modification. *2-p-Dimethylaminobenzal-3-hydroxy-4-carbethoxy-5-methylpyrrole* (H) or its tautomer was obtained analogously from the appropriate reagents in alc. soln. and pptn. with H_2O ; yellow needles, m. 214° , gives a bluish red color with $FeCl_3$, an intense color with dil. HCl or H_2SO_4 in alc. or Me_2CO , is insol. in $CHCl_3$ and Et_2O . C when dissolved in Ac_2O with a liberal pinch of $AcONa$ gives *acetyl-3-hydroxy-4-carbethoxy-5-methylpyrrole* (I), needles, m. 123° , sol. in $AcOH$, $CHCl_3$, Me_2CO and pyridine. A well defined Bz analog could not be obtained. Azo derivatives of C were prep'd. by using diazotized solns. of *aniline*, *p-dichloroaniline* and *p-nitroaniline* and *diazobenzenesulfonic acid*. They are here designated as J, K, L, and M, resp. J crystals as yellow needles from $CHCl_3$, slightly sol. in alc., m. 240° . The coupling may be carried out with alc. or H_2O suspensions of the pyrrole or in $AcOH$. K (prep'd. with an alc. suspension of C) forms yellow crystals, m. 265° . L (prep'd. with an $AcOH$ soln. of C) forms yellow needles slightly sol. in alc. $CHCl_3$, Et_2O and $AcOH$. M (prep'd. with an $AcOH$ soln.) forms fine yellow needles. A series of compds. was prep'd. by coupling *o*-nitrophenylsulfur chloride with various pyrroles in C_6H_6 . *2,4-Dimethyl-3-acetyl-4-thio-o-nitrophenylpyrrole* (N), greenish comp'd., m. 252° , slightly sol. in alc. $AcOEt$, C_6H_6 , benzine, $CHCl_3$, Me_2CO and 50% H_2SO_4 , insol. in 25% H_2SO_4 . *2,4-Dimethyl-3-thio-o-nitrophenyl-5-acetylpyrrole* (O), greenish substance, m. $217-8^\circ$ when crystd. from alc., somewhat sol. in $AcOEt$, C_6H_6 , alc., Me_2CO , $AcOH$, $MeOH$, sol. in $CHCl_3$, slightly sol. in Et_2O , insol. in petroleum ether. *2,3,5-Trimethyl-4-thio-o-nitrophenylpyrrole* (P) crystals from alc. in brick-red tufts, m. $151-2^\circ$, easily sol. in alc., Et_2O , Me_2CO , $AcOEt$, $CHCl_3$, $AcOH$, C_6H_6 , somewhat sol. in petroleum ether, insol. in H_2O . *2,4-Dimethyl-3-carbethoxy-5-thio-o-nitrophenylpyrrole* (Q), yellow, octahedral crystals, m. $191-2^\circ$ when crystd. from alc., sol. in $AcOEt$, Me_2CO , $CHCl_3$, pyridine, less sol. in alc., C_6H_6 , $AcOH$ and Et_2O , insol. in petroleum ether. *2,5-Dimethyl-3-carbethoxy-4-thio-o-nitrophenylpyrrole* (R) (from alc.), fine yellow prisms, m. 189° , sol. in $AcOEt$, $AcOH$, $MeOH$, Me_2CO , C_6H_6 , less sol. in alc. and Et_2O , insol. in petroleum ether and H_2O . Derivs. of pyrroles contg. methine groups in which 2 pyrrole groups were linked by means of 1 or 2 S atoms were prep'd. by the action of S_2Cl_2 and SCl_2 . *Di-3,5-dimethyl-4-carbethoxypyrryl disulfide* (S) (the reaction was carried out in Et_2O) forms bright yellow prisms (from $CHCl_3$), m. 195° , sol. in alc., $AcOEt$, $CHCl_3$, Me_2CO , $AcOH$, C_6H_6 , insol. in Et_2O , petroleum ether and H_2O . *Di-2,4-dimethyl-3-carbethoxypyrryl sulfide* (T) (the reaction was carried out in Et_2O), colorless, long, needles, m. 197° ; the initial product was contaminated with the disulfide from which it was freed by dissolving in alc., adding H_2O until turbidity occurred (due to the disulfide), warming and filtering. From the filtrate the pure comp'd. seps.; it is sol. in alc., $AcOEt$, $CHCl_3$, C_6H_6 and $AcOH$. *Di-2,5-dimethyl-3-carbethoxypyrryl disulfide* (U) (the reaction was carried out in Et_2O) m. 272° (crystd. from alc.), sol. in alc., $AcOH$, slightly sol. in $CHCl_3$, $AcOEt$ and Me_2CO , insol. in C_6H_6 , Et_2O and petroleum ether. *Di-2,5-dimethyl-3-carbethoxypyrryl sulfide* (V) (the reaction was carried out in $CHCl_3$) forms yellow, quadratic needles, m. 224° (crystd. from alc.). As prep'd. it was mixed with the disulfide, from which it was freed by adding alc. and decanting; the lighter disulfide is thus sepd. *Di-2,4-dimethyl-5-acetylpyrryl disulfide* (W) (the reaction was carried out in $CHCl_3$) forms prisms, m. 317° (crystd. from dil. $AcOH$), slightly sol. in alc. $CHCl_3$, $AcOEt$, Me_2CO , more sol. in $AcOH$, insol. in Et_2O , C_6H_6 , $MeOH$, petroleum ether and CS_2 . *Di-2,4-dimethyl-5-acetylpyrryl sulfide* (X) (the reaction was carried out in $CHCl_3$) m. 315° (crystd. from dil. $AcOH$). R. L. S.

The substituted thioureas. III. The synthesis of thiazolidine and thiazane derivatives. F. B. DAINS, R. Q. BREWSTER, J. S. BLAIR AND W. C. THOMPSON. *J. Am. Chem. Soc.* **44**, 2637-43 (1922).—2,3-Disubstituted thiazolidines were prep'd. by the addn. of mustard oil to the arylallylamines and the subsequent rearrangement of

the thiourea: $\text{RNHC}_2\text{H}_5 + \text{RNCS} = \text{RNHCNRC}_2\text{H}_5 = \text{S.C}(\text{:NR}).\text{NR}.\text{CH}_2.\text{CH}_3.\text{CHMe}.$

Allylaniline, from Na formanilide and allyl bromide or iodide, does not rearrange when heated 8 hrs. at 250° in a sealed tube, the only products obtained being unsatd. hydrocarbons, PhNH_2 , PhNHC_2H_5 and a large amt. of non-hasic tarry material; *hydrochloride*, deliquescent crystals, m. 110°; *acid oxalate*, m. 120°. α -Allyl- α,β -diarylthiureas and their m. p.: α,β -diphenyl, 91°; α -phenyl- β -p-bromophenyl, 123°; α -phenyl- β -p-tolyl, 107°; α -p-tolyl- β -phenyl, 91.5°; α -p-tolyl- β -p-bromophenyl, 121°; α,β -di-p-tolyl, 113°. *2-Arylimino-3-aryl-5-methylthiazolidines*: 2,3-Diphenyl, 98° (*picrate*, m. 168-9°); 2-p-bromophenyl-3-phenyl, 106°; 2-p-tolyl-3-phenyl, oil (*picrate*, m. 188°); 2-phenyl-3-p-tolyl, 72-3° (*picrate*, m. 164-6°); 2-p-bromophenyl-3-p-tolyl, 81°; 2,3-di-p-tolyl, oil (*picrate*, m. 140°); Arylaminoethanols combine smoothly with mustard oils to form thioureas which, when heated alone or with halogen acids, react in the enol form with loss of H_2O and consequent thiazole formation: $\text{RNHCH}_2\text{CH}_2\text{OH} + \text{RNCS} = \text{RN:C}(\text{SH})\text{NRCH}_2\text{CH}_2\text{OH} = \text{S.C}(\text{:NR}).\text{NR}.\text{CH}_2.\text{CH}_2.$ The arylaminoethanols are best

prepd. by heating $\text{ClCH}_2\text{CH}_2\text{OH}$ with 2 mols. of the amine several hrs. at 120-30°. *o-Tolylaminoethanol*, viscid oil, n_D^{20} 1.72°, gives with 1 mol. PhNCS on standing or warming gently, alone or in alc., the thiourea, flakes from alc., m. 108°, which, heated a short time with concd. HCl or HBr , yields 2-phenylimino-3-phenylthiazolidine, identical with the product prepd. from $(\text{CH}_3\text{Br})_2$ and $\text{CS}(\text{NHPh})_2$ (Will, *Ber.* 14, 1490(1881)); it is also obtained in good yield by heating the aminoethanol with 2 mols. PhNCS alone for several hrs. at 110°. *2-Arylimino-3-arylthiazolidines*: 2-o-Tolyl-3-phenyl, 94°; 2-p-tolyl-3-phenyl, 113°; 2,3-di-o-tolyl, 105°; 2-phenyl-3-o-tolyl, 92°. The ethanolthiureas hoiled in C_6H_6 with yellow HgO give the corresponding ring O derive.; in this way was prepd. 2-phenylimino-3-phenyloxazolidine, m. 124°, also obtained from $\text{PhNHCONPhCH}_2\text{CH}_2\text{OCONHPh}$ hoiled with concd. HBr . Aryl- γ -hydroxypropylamines easily add aryl isothiocyanates and the resulting thioureas give with halogen acids *m*-thiazanes, $\text{S.C}(\text{:NR}).\text{NR}.\text{CH}_2.\text{CH}_2.\text{CH}_2.$ The arylaminoethanols were

prepd. by heating $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{OH}$ with 2 mols. of the amine several hrs. at 130°. γ -Hydroxypropyl-p-tolylamine, thick oil, n_D^{20} 1.85-90°, n_D^{25} 200-5°. α -Propanol- α,β -diarylthiureas: α,β -Diphenyl, 130°; α,β -di-p-tolyl, 142°; α -p-tolyl- β -phenyl, 146°; α -phenyl- β -p-tolyl, 127°. *2-Arylimino-3-arylthiazanes*: 2,3-Diphenyl, 139°, identical with the compd. prepd. from $\text{CS}(\text{NHPh})_2$ and $\text{CH}_2(\text{CH}_2\text{Br})_2$ (Foerster, *Ber.* 21, 1884(1888), gives 123° as the m. p.); 2,3-di-p-tolyl, 111°; 2-phenyl-3-p-tolyl, 139°; 2-p-tolyl-3-phenyl, 94°. Epichlorohydrin and *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$ in alc. give $\text{MeC}_6\text{H}_4\text{NHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$, m. 85°, which, heated with *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$, yields $\text{HOCH}(\text{CH}_2\text{NHC}_6\text{H}_4\text{Me})_n$, m. 116° (Cohn and Friedländer, *Ber.* 37, 3035(1904), give 81-2° and 113° as the m. ps. of the 2 compds.); the 2nd compd. is also obtained by heating $\text{HOCH}(\text{CH}_2\text{Cl})_2$ with 4 mols. $\text{MeC}_6\text{H}_4\text{NH}_2$ 5 hrs. at 140-50°. Amines of the type $\text{RNHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$ form with mustard oils the thioureas which cannot be isolated, owing to the loss of HCl and formation of 2-arylimino-3-aryl-5-hydroxythiazanes, of which the following were prepd.: 2-Phenyl-3-p-tolyl, 175° (*hydrochloride*, m. 187°); 2,3-di-p-tolyl, 142° (*hydrochloride*, m. 204°; *picrate*, m. 195°); 2-phenyl-3-p-anisyl, 157° (*picrate*, m. 135°); 2-phenyl-3-p-chlorophenyl, 171°; 2,3-diphenyl, 175° (*picrate*, m. 150°), also obtained from $\text{CS}(\text{NHPh})_2$ and epichlorohydrin heated some hrs. in Me_2CO ; 6 g. of the diphenylthiazane heated 3 hrs. at 120° with 4.5 g. PhNCS gives 5 g. of the *phenylurethan*, $\text{S.C}(\text{:NPh}).\text{NPh}.\text{CH}_2.\text{CH}(\text{OCONHPh}).\text{CH}_2$, m. 185°. C. A. R.

Some δ -ketonic nitriles and their relation to cyclic compounds. I. E. P. KOHLER, ALICE GRAUSTEIN AND D. R. MERRILL. *J. Am. Chem. Soc.* 44, 2536-56(1922).—By

adding $\text{NCCH}_2\text{CO}_2\text{Et}$, $\text{NCCH}_2\text{CONH}_2$, $\text{CH}_3(\text{CN})_2$, PhCH_2CN and similar substances to unsatd. ketones it is possible to obtain a great variety of closely related δ -ketonic nitriles which change more or less readily into hydropyridine derivs. This paper deals with the substances obtained by adding $\text{NCCH}_2\text{CO}_2\text{Me}$ (A) to PhCH:CHCOPh (B) and $p\text{-ClC}_6\text{H}_4\text{COCH:CHPh}$ (C). The rearrangement of the open-chain addn. product (D), $\text{MeO}_2\text{CCH}(\text{CN})\text{CHRCH}_2\text{COR}'$, into the cyclic compd. (E), $\text{MeO}_2\text{CCH.CO.NH.CR}':\text{CH.CHR}$, takes place with great ease when

solns. of the D in indifferent media are satd. with dry HCl or with HBr; if the amt. of solvent is small the change is almost quant. and when HBr is used the reaction is completed in a few hrs. As the process is reversible, the D and the isomeric E generally give the same products in reactions occurring in the presence of acids. While the rearrangement takes place readily in glacial AcOH, as well as in CHCl_3 and CCl_4 , it is completely inhibited by AcCl or Ac_2O ; a trace of H_2O is therefore essential and the reaction probably occurs through the amide, $\text{MeO}_2\text{CCH}(\text{CONH}_2)\text{CHRCH}_2\text{COR}'$, as an intermediate product. The rearrangement can also be effected by brominating the D; this is an exceedingly involved process and unless precautions are taken to prevent the isomerizing action of the HBr formed a whole series of Br derivs. of both the D and E is obtained. The bromination can be regulated by providing a reagent which will combine with the HBr as fast as formed or by brominating in glacial AcOH. The concn. of the HBr can be kept very low by brominating very slowly in the presence of a large excess of finely powdered fused KOAc. Under these conditions the products are $\text{MeO}_2\text{CCBr}(\text{CN})\text{CHPhCH}_2\text{COR}$ (F), $\text{MeO}_2\text{CCBr}(\text{CN})\text{CHPhCHBrCOR}$ (G) and $\text{PhC.CH}=\text{CR}$

$\text{MeO}_2\text{CC.CBr:N}$ (H). In the presence of an adequate amt. of KOAc, E is the main product, with only a trace of H, while in glacial AcOH H is obtained almost exclusively; H is also formed quant. by satg. E in CHCl_3 with HBr. The passage of A into H is doubtless always through the unstable $\text{MeO}_2\text{CCBr}(\text{CBr:NH})\text{CHPhCH:C}(\text{OH})\text{OR}$. The reaction is an uncommonly clean one and constitutes a new pyridine synthesis. In the presence of a small amt. of NaOMe A combines as readily as $\text{CH}_2(\text{CO}_2\text{Me})_2$ with unsatd. ketones, but besides the normal 1:1 addn. product it invariably gives a "trimol." compd. of 1 mol. A with 2 mols. of the ketone, formed secondarily by addn. of the normal product to a 2nd mol. of the ketone. In order to confine the reaction as far as possible to the 1st stage, it is important to use very dry MeOH and the smallest possible amt. of NaOMe. Thus, 208 g. B and 125 g. A in 300 cc. MeOH (distd. from $\text{Mg}(\text{OMe})_2$) at 50° treated dropwise with NaOMe until perceptibly alk. to litmus and boiled 1 hr. gives 257 g. methyl γ -benzoyl- β -phenyl- α -cyanobutyrate (D), prisms from Et_2O , m. 76° , has a great tendency to sep. as an oil unless seeded, and 3.5 g. of the trimolecular product, $\text{MeO}_2\text{CC}(\text{CN})(\text{CHPhCH}_2\text{COPh})_2$, cubes from $\text{CHCl}_3\text{-MeOH}$, m. about 226° . Methyl γ -*p*-chlorobenzoyl- β -phenyl- α -cyanobutyrate (D), obtained in 87% yield from C, needles from MeOH, m. 126° ; trimolecular product, prisms, m. $230\text{--}2^\circ$. $\text{MeCH}(\text{CN})\text{CO}_2\text{Me}$ with C gives a mixt. in varying proportions of 2 stereoisomeric methyl γ -*p*-chlorobenzoyl- β -phenyl- α -methyl- α -cyanobutyrate, thin plates from MeOH, m. 108° and 92° , converted by allowing to stand several days in dry MeOH satd. with HCl into dimethyl γ -*p*-chlorobenzoyl- β -phenyl- α -methylmalonate [dimethyl methyl β -*p*-chlorobenzoyl- α -phenylethylmalonate], m. 106° , also obtained from $\text{MeCH}(\text{CO}_2\text{Me})_2$ and C. The D can be hydrolyzed at will to ester acids, dibasic acids and CN acids. The 1st reaction must be carried out in an acid medium, best H_2SO_4 in glacial AcOH; for the 2nd reaction it is best to go to the ester of the dibasic acid and hydrolyze this with bases; the 3rd reaction must be effected in bases and unless the conditions are properly selected the addn. reaction is in part reversed and the principal products are

the dimol. compd., $\text{NCCH}_2\text{CO}_2\text{H}$ and various other substances formed by the action of the alkali on the unsatd. ketone. γ -Benzoyl- β -phenyl- α -carbomethoxybutyric acid (2.7 g. from 3.5 g. of the D allowed to stand several days in 1 cc. concd. H_2SO_4 and 5 cc. AcOH), friable needles from C_6H_6 , m. 160° (slow decompn.), decomp. freely above 180° , forms $\text{BzCH}_2\text{CHPhCH}_2\text{CO}_2\text{Me}$ when heated to 200° . γ -Benzoyl- β -phenyl- α -cyanobutyric acid (12 g. from 5 g. KOH and 15 g. D, each in 100 cc. MeOH, brought together in a freezing mixt. and allowed to stand 24 hrs. in the ice box), friable needles from C_6H_6 , m. about 160° (slight decompn.), gives at 200° γ -benzoyl- β -phenylbutyronitrile, needles from MeOH, m. 76° , rapidly hydrolyzed by boiling alc. KOH to $\text{BzCH}_2\text{CHPhCH}_2\text{CO}_2\text{H}$, is unchanged when allowed to stand a week in concd. CHCl_3 or CCl_4 soln. satd. with HCl or HBr, gives with Br in CHCl_3 a cryst. mono-Br deriv. which readily loses HBr when boiled with KOAc in MeOH. Methyl 2-keto-4,6-diphenyltetrahydropyridine-3-carboxylate (E) (57 g. from 60 g. D in CCl_4 satd. with HBr and allowed to stand a few hrs.), needles from MeOH, m. $165-6^\circ$, does not reduce KMnO_4 in Me_2CO at room temp. but rapidly decolorizes Br in CHCl_3 even at -20° ; when it is warmed in MeOH with a little concd. H_2SO_4 or satd. with HCl, the ring opens and the di-Me ester of the corresponding dibasic acid is formed; free acid of E, from E and dil. alc. KOH, cubes from Me_2CO -petr. ether, m. about 130° (free effervescence) in a capillary but gives off CO_2 far below this temp. in open vessels; at 150° it yields 2-keto-4,6-diphenyltetrahydropyridine, flat needles from MeOH, m. 130° , does not reduce cold KMnO_4 , but reacts readily with Br. Methyl 2-keto-4-phenyl-6-p-chlorophenyltetrahydropyridine-3-carboxylate (yield, 90%), m. 204° . All the tetrahydropyridine derivs. react with Br with great ease. If the reaction is carried out with sufficient care mono-Br derivs. are obtained almost exclusively; if it is carried out at too high a temp. the product is contaminated with the corresponding dihydropyridine deriv. and when Br is used in excess corresponding amts. of more highly brominated compds. are formed. Methyl 2-keto-4,6-diphenyl-5-bromotetrahydropyridine-3-carboxylate (59 g. from 50 g. E in 150 cc. CHCl_3 treated at 0° with a 50% soln. of Br in CHCl_3 until the color persists (almost exactly 1 mol. Br is required), heated to boiling and immediately cooled), prisms with strong greenish yellow fluorescence from CHCl_3 -MeOH, m. $160-1^\circ$; allowed to stand several days in MeOH satd. with HBr, it gives $\text{BzCHBrCHPhCH}(\text{CO}_2\text{Me})_2$; 12 g. in boiling MeOH with 1 g. Na in MeOH gives 3.8 g. methyl 2-hydroxy-4,6-diphenylpyridine-3-carboxylate, hydrolyzed by KOH in boiling aq. MeOH to the acid, fine yellow needles from MeOH, m. 253° (decompn.), which, heated 15 min. at 200° in *vacuo*, gives 2-hydroxy-4,6-diphenylpyridine, very pale yellow plates from MeOH, m. $209-10^\circ$. The mono-Br ester (38 g.) with 16 g. Br in CHCl_3 gives the 3,5-dibromo ester (never more than 50%), prisms from CHCl_3 -petr. ether, m. about 160° (decompn.); rapidly satd. in MeOH with HBr and cooled in a freezing mixt. it gives NH_4Br , $\text{BzCHBrCHPhCBr}(\text{CO}_2\text{Me})_2$ and γ -benzoyl- α , γ -dibromo- α -carbomethoxy- β -phenylbutyramide, tufted needles from CHCl_3 , decomp. about 180° ; a stereoisomer, minute needles from MeOH, m. about 140° (decompn.), is formed when the CHCl_3 soln. in which the di-Br ester has been prepd. is allowed to stand in contact with air for some time before the HBr is washed out. Neither of the stereoisomers could be converted into the corresponding diester but both undergo on heating the change into furan derivs. characteristic of γ -Br esters, yielding the same 3-bromo-3-cyano-4-phenyl-5-benzoyl- α -furan [3-bromo-3-cyano-4-phenyl-5-benzoyl-2-ketotetrahydrofuran], m. 275° . When the mono-Br ester is brominated in boiling CHCl_3 or when solns. in which it has been brominated are heated before the HBr has been completely removed, the di-Br compd. loses HBr and the chief product is methyl 1-hydroxy-3,5-diphenyl-4-bromopyridine-3-carboxylate, fine needles from CHCl_3 -MeOH, m. $238-40^\circ$, does not undergo further bromination, even when boiled with Br, but readily forms a *perbromide*, ruby-colored crystals from CHCl_3 ,

begins to dissociate about 140°, rapidly regenerates the mono-Br compd. with SO₂ or KI; free acid of the Br ester, pale yellow prisms from MeOH, m. about 270° (decompn.), gives at 280° *in vacuo* 1-hydroxy-4,6-diphenyl-3-bromopyridine, fine yellow needles from alc., m. 278°. Methyl 2-keto-4-phenyl-5-bromo-6-p-chlorophenyltetrahydropyridine-3-carboxylate, obtained in 98% yield from 75 g. of the D in CHCl₃ satd. with HBr, allowed to stand overnight, treated with 38.5 g. Br in CHCl₃ and boiled 20 min., needles from C₆H₆, m. 194°. 3,5-Dibromo ester, greenish prisms, m. 183°. Methyl 2-hydroxy-4-phenyl-6-p-chlorophenylpyridine-3-carboxylate, flat needles with blue fluorescence from MeOH, m. 262°, sol. in concd. alkalies, reprecipitated by acids. Methyl α-bromo-α-cyano-β-phenyl-γ-benzoylbutyrate (F) (32 g. from 50 g. D in CHCl₃ with 70 g. KOAc very slowly treated, with vigorous stirring, with 28 g. Br in CHCl₃), diamond-shaped plates from MeOH, m. 130°, loses HBr with formation of a cyclopropane deriv. when digested with KOAc in MeOH, is stable up to 200°; allowed to stand for a week in MeOH satd. with HBr it remains largely unchanged, yielding only a small amt. of BzCH₂CHPhCH(CO₂Me). Together with F there is also formed methyl α,γ-dibromo-α-cyano-β-phenyl-γ-benzoylbutyrate (G) (easily prepd. by adding the requisite amt. of Br to F in boiling CHCl₃), coarse needles from MeOH, m. 177–9°, decomps. at a slightly higher temp., yields a cyclopropane deriv. with KI. Methyl α-bromo-α-cyano-β-phenyl-γ-p-chlorobenzoylbutyrate is obtained in 2 isomeric forms, tables, m. 91–2°, and prisms, m. 123°, both of which behave alike in all reactions. α,γ-Dibromo ester, fine needles from alc., m. 193°. When the bromination is carried out in glacial AcOH, about 92% of the product is H with about 3% of G and no F. Methyl 2-bromo-4,6-diphenylpyridine-3-carboxylate (H) (36 g. from 30 g. D in hot glacial AcOH treated dropwise with 10 g. Br), 6-sided prisms or coarse needles with blue fluorescence, m. 147°, also obtained in good yield from F in CHCl₃ or AcOH satd. with HBr and allowed to stand overnight, hydrolyzed by boiling concd. aq. alk. KOH to the free acid, needles from MeOH, m. 206–8° (decompn.), cannot be reconverted into H with MeOH and HCl but can be so esterified by digesting the Ag salt with an excess of MeI. Methyl 2-bromo-4-phenyl-6-p-chlorophenylpyridine-3-carboxylate, fluorescent striated plates from MeOH, m. 106°. Methyl α-chloro-α-cyano-β-phenyl-γ-p-chlorobenzoylbutyrate, formed almost quant. from the D in CHCl₃ at 0° treated with slightly more than 1 equiv. of Cl in CCl₄, is obtained in 2 stereoisomeric forms, prisms, m. 106°, and plates, m. 80°; both lose HCl with equal ease to KOAc with formation of the same cyclopropane deriv. but they behave differently towards HBr; the high melting isomer boiled several hrs. in CHCl₃ satd. with HBr gives methyl 2-keto-3-chloro-4-phenyl-6-p-chlorophenyltetrahydropyridine-3-carboxylate, needles from MeOH, m. about 197° (decompn.), while the low melting isomer gives mainly the same chromotetrahydropyridine deriv. as is obtained by rearranging the D and then brominating the product. Methyl 2-hydroxy-4-phenyl-5-chloro-6-p-chlorophenylpyridine-3-carboxylate, from 5 g. of the E in CHCl₃ with 20 cc. of a satd. CCl₄ soln. of Cl, prisms from alc., m. 196°. Methyl 2-keto-3,4,5-trichloro-4-phenyl-6-p-chlorophenyltetrahydropyridine-3-carboxylate, from a satd. CCl₄ soln. of Cl (275 g.) and 10 g. E in CHCl₃ in direct sunlight (yield, 96%), needles, loses Cl below the m. p. which therefore depends on the rate of heating, being about 260° when heated in a capillary in the usual way, loses 2 atoms of Cl and yields the preceding compd. when boiled with Zn dust in MeOH. The cyclopropane derivs. were obtained by heating the F *in vacuo* or by treating them with KOAc, by removing HCl from the corresponding Cl compds. or by removing Br from the G with KI. Methyl 1-cyano-2-phenyl-3-benzoylcyclopropane-carboxylate is obtained in 3 isomeric forms: (1) prisms, m. 178–80°, from E on heating or treating with KOAc in MeOH, does not reduce KMnO₄ but is reduced by Zn dust in boiling aq. MeOH-MeOAc to D; (2) coarse needles or prisms, m. 106°, obtained by heating with KOAc in MeOH the oily residues from the bromination of D in CHCl₃;

(3) needles, m. 110° , obtained in 2.1 g. yield from 4 g. G shaken 24 hrs. in MeOH with the calcd. amt. of KI and an excess of Hg. Free acid, from the 106° ester with NaOMe in wet Et_2O , prisms, m. about 230° (decompn.). Methyl 1-cyano-2-phenyl-3-p-chlorobenzoylcyclopropanecarboxylate is obtained in 2 forms; long fine needles or cubes, m. 132° , obtained in 80% yield from D in CHCl_3 with Br and KOAc; (2) long needles, m. 180° , obtained in 90% yield from the G with KI in MeOH. Allowed to stand several days in MeOH with KOAc the high- is converted into the low-melting isomer. II. E. P. KOHLER AND B. F. SOUTHER. *Ibid* 2903-14.—In a continuation of the work described in the 1st paper, $\text{NCCH}_2\text{CONH}_2$ and NCCH_2CN have been added to PhCH:CHCOPh and the resulting products, $\text{NH}_2\text{COCH}(\text{CN})\text{CHPhCH}_2\text{COPh}$ (A) and $\text{NCCH}(\text{CN})\text{CHPhCH}_2\text{COPh}$ (B), compared with that (C) obtained from $\text{NCCH}_2\text{CO}_2\text{Me}$. The behavior of these 3 closely related substances towards most reagents is surprisingly different and, in fact, it is only on esterification that they behave alike. Thus, while all 3 form cyclic compds. when subjected to the action of halogen acids in indifferent media, C forms a tetrahydropyridine deriv. by mol. rearrangement; A does also, but in accord with the mechanism proposed in the 1st paper the ring formation involves the amide in place of the CN group and the process is accompanied by loss of H_2O ; B gives a mixt. composed almost entirely of pyridine and hexahydropyridine derivs., with only a trace of the tetrahydro compd., and yields a similar mixt. with alc. KOH. These mixts. are doubtless due to a series of reactions, starting with the addn. of halogen acid or alcoholate to one of the CN groups and ending with the spontaneous oxidation and reduction of an intermediate dihydropyridine deriv. The results in the main confirm the plausible view that such oxidation-reduction reactions are associated with the extraordinary activity of H which is in combination with atoms flanked on both sides by unsatd. groups, but they do not support the conclusion that hydropyridine derivs. are incapable of reacting in all possible desmotropic forms (cf. Knoevenagel, *Ber.* 36, 2813(1903)). α -Cyano- β -phenyl- γ -benzoylbutyramide (A) (yield, 72.5%), needles or prisms from MeOH, m. $161-3^{\circ}$, also obtained from C with NH_3 . Butyronitrile (B), needles or prisms from EtOH or CCl_4 , m. $125-6^{\circ}$. In MeOH the halogen acids esterify A to the ester previously obtained by adding $\text{CH}_3(\text{CO}_2\text{Me})_2$ to PhCH:CHCOPh, but in CHCl_3 or CCl_4 they rapidly convert it, almost quant., into 2-keto-3-cyano-4,6-diphenyltetrahydropyridine (D), needles from $\text{C}_6\text{H}_5\text{-EtOH}$, m. 220° , sol. in concd. H_2SO_4 with amber color and repptd. unchanged if at once poured upon ice, but if kept 8-10 hrs. it hydrolyzes to the 3-carbamyl derivative (D'), prisms from Me_2CO contg. a few drops of NH_4OH , m. $181-2^{\circ}$, sol. in concd. H_2SO_4 , yielding mainly the 3- MeCO_2C deriv., m. 166° (cf. preceding abstr.) when poured into cold MeOH. 1-Hydroxy-3-cyano-4,6-diphenylpyridine (E) (2.7 g. from 5 g. D in AcOH slowly treated with a concd. aq. soln. of 2.7 g. NaNO_2 and allowed to stand several days), greenish yellow plates from AcOH, m. $313-5^{\circ}$, gives 2-hydroxy-4,6-diphenylpyridine with KOH in boiling MeOH. From 10 g. D shaken 2 weeks with 30 cc. of concd. alc. NH_3 are obtained 4.1 g. E and 3.2 g. 2-keto-3-cyano-4,6-diphenylpiperidine (F), fine needles with intense blue fluorescence from Me_2CO -petr. ether, m. $188-9^{\circ}$. Satd. in CHCl_3 with HCl, 3 g. B gives 0.5 g. F and 1 g. 2-chloro-3-cyano-4,6-diphenylpyridine, also obtained in 85% yield from E in POCl_3 heated a few min. on the H_2O bath with a slight excess of PCl_5 , long silky filaments from MeOH, m. 154.5° . 2-Bromo analog, obtained in 6.3 g. yield from 15 g. B in CHCl_3 with HBr, silky needles from CHCl_3 -MeOH, m. $169-70^{\circ}$; at the same time there is formed 5.5 g. 2-keto-3-carbamyl-4,6-diphenylpiperidine, minute needles from AcOH, m. about 170° when dipped into a bath at this temp., m. $230-2^{\circ}$ when heated in the ordinary way, is also obtained quant. by hydrolysis of F with acids, gives in MeOH with HCl methyl 2-keto-4,6-diphenylpiperidine-3-carboxylate, needles from Me_2CO -petr. ether, sinters 173° , m. 177° . While A is converted by alkalis for

the most part into D', the only other product being a "trimol." compd., B gives only pyridyl ethers (less than 50%) and uncrystallizable oils with alc. KOH. Thus, 3 g. B allowed to stand 24 hrs. in 20 cc. of 10% KOH in MeOH and 5 cc. H₂O yields 1 g. 2-methoxy-3-cyano-4,6-diphenylpyridine, silky needles from MeOH, m. 110°, also obtained in 4.2 g. yield from 5.9 g. of the 2-Br compd. boiled 6 hrs. with a slight excess of NaOMe. 2-Ethoxy homolog, needles, m. 112°. The rearrangement of A into cyclic compds. takes place so readily that only cyclic Br compds. are obtained from it, even when the bromination is carried out in the presence of KOAc, while 5 g. B with 5 g. KOAc treated in CHCl₃ with 1 cc. Br gives 5 g. α -bromo- α , α -dicyano- β -phenyl- γ -benzoylbutyronitrile, needles from MeOH, m. 126-7°. The principal product of the action of 1 equiv. Br on A, in CHCl₃, in the presence of a large excess of KOAc or in AcOH is 2-keto-3-cyano-4,6-diphenyl-5-bromoletrahydropyridine (G), fine needles, m. about 165° as detd. by the "dip" method but when heated in the ordinary way it loses HBr below the m. p. and therefore does not m. below 312°, the m. p. of 2-hydroxy-3-cyano-4,6-diphenylpyridine, into which it is also rapidly converted by boiling with NaOMe and slowly by KOAc in boiling alc. The 5-chloro analog, long needles, m. 178-81°, is the 1st product of the action of PCl₅ on D. 3,5-Dibromo compound, from A, D(?) or G with excess of Br in hot CCl₄, yellow plates, decomps. about 195° (effervescence), loses HBr so readily that it is difficult to obtain pure. 2-Hydroxy-3-cyano-5-bromo-4,6-diphenylpyridine, m. 303-6° (charring), one of the by-products in the bromination of A in AcOH, is easily prepd. from G in AcOH slowly treated with NaNO₂; with POCl₃ and PCl₅ it gives the 2-chloro compound, pale yellow plates from Me₂CO-petr. ether, m. 181-2°. 2,5-Dibromo-3-cyano-4,6-diphenylpyridine, one of the products of the bromination of B with an excess of Br in the presence of KOAc and also obtained by brominating the 1-Br compd. in sunlight, seps. from Me₂CO-petr. ether in pale yellow prisms, m. 189-90°.

C. A. R.

Formaldehyde derivatives of 2,5-diketopiperazine. ÉMILE CHERBULIEZ AND ÉMANUEL FEER. *Helvetica Chim. Acta* 5, 678-87(1922).—Diketopiperazine (A) was used as the basis of this series, since it is the simplest α -NH₂ acid, whose N is present wholly as substituted amide N, and therefore the simplest analog of the proteins. The possibility and character of HCHO addition products to the N atoms of this type are demonstrated. 1,4-Dihydroxymethyl-2,5-diketopiperazine (B) $\text{HOCH}_2\text{N}(\text{CO}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{OH})\text{CO}(\text{CH}_2)_2\text{N})$, prepd. by dissolving A in 6 parts

HCHO (after 24 hrs.' standing the yield is 90%), prisms from MeOH, m. 178° (decompn.), sol. in H₂O, EtOH, pyridine, insol. in Et₂O, decomps. in concd. NH₄OH. In small portions, 2.2 mols. 5 N NaOH, with shaking and cooling, is added to 3.4 g. B suspended in 10 cc. H₂O and 2.2 mol. Me₂SO₄. After letting stand 0.5 hr., neutralizing and concg. 1,4-dimethoxymethyl-2,5-diketopiperazine (C) is extd. from the residue with EtOAc; colorless plates from Et₂O, m. 99-100°, sol. in H₂O, EtOAc and EtOH, neutral and stable in aq. soln., completely hydrolyzes with boiling HCl. Hydrochloride m. 165-6°. Hydrochloride of ethyl ether m. 144°. B, heated for 0.5 hr. with 2 mols. BaO in pyridine and poured into H₂O, yields 50% of 1,4-dibenzoxymethyl-2,5-diketopiperazine, plates, m. 182°, hy pptn. from pyridine with EtOH, insol. in H₂O and Et₂O, completely hydrolyzes by boiling with concd. NaOH. 0.5 g. B in 5 g. MeOH condenses with 0.6 g. piperidine and on concn. and cooling yields 50% of 1,4-dipiperidomethyl-2,5-diketopiperazine, recrystd. from Me₂CO, large prisms, m. 156-7°, sol. in H₂O and MeOH, completely hydrolyzes with boiling H₂O or EtOH. On adding 2 g. B to a suspension of 6 g. PCl₅, 5 g. CCl₄ and 5 g. AcCl, 1,4-dichloromethyl-2,5-diketopiperazine (D) crystals on cooling (91% yield), hard white crystals from CHCl₃, sinters 140°, m. 162° (decompn.), sol. in C₆H₆, Me₂CO, HOAc, Et₂O, forms the hydrochloride of the quaternary base on addn. of pyridine. By heating D with MeOH, C is formed; with EtOH, 1,4-diethoxymethyl-

L. E. GILSON

Study of catalytic actions at solid surfaces. VIII. The action of sodium carbonate in promoting the hydrogenation of phenol (ARMSTRONG AND HILDITCH) 2. Catalytic hydrogenation and the potential of the hydrogen electrode (CONANT AND CUTLER) 2.

Metalddehyde. H. DANNEEL and E. LUSCHER. U. S. 1,432,387, Oct. 17. A metalddehyde which is stable at high temps. and in which residual traces of catalyst are rendered harmless is prepd. by removing paraldehyde from crude metalddehyde by use of a solvent or by vacuum distn. and converting the residual H_2SO_4 or other catalyst into $BaSO_4$ or other harmless compd. Cf. C. A. 16, 3315.

Chlorinating methane. HOLZVERKOHLEUNGS-INDUSTRIE AKT.-GES. AND K. RÓKA. Brit. 186,270, Nov. 22, 1921. In the chlorination of CH_4 , steam is employed as a diluent to the reacting gases to moderate the violence of the reaction and at the same time to supply, if necessary, the heat for its initiation. In general, 2-5 vols. of steam per unit vol. of Cl are used and temps. above 650° are avoided, owing to the decompn. of steam and formation of oxides of C. Catalysts such as chlorides of Cu, Fe, and the alk. earth metals may be employed, with or without porous carriers. The relative proportions of the reacting gases are dependent on the dimensions of the reaction tubes and upon the products required. Examples are given in which the formation, resp., of $MeCl$, methylene dichloride, CH_2Cl_2 , and of CCl_4 is promoted.

Chlorinating liquid paraffin hydrocarbons. G. T. KOCH. U. S. 1,432,761, Oct. 24. Chlorination of normally liquid hydrocarbons in the liquid phase is effected by the action of Cl gas in the presence of finely divided activated C, silica gel or pumice. The C may be impregnated with Ni.

Reaction of ethyl acetate with amyl alcohol. J. A. STEFFENS. U. S. 1,433,308, Oct. 24. $AmOAc$ is formed by reaction between $EtOAc$ and $AmOH$ in the presence of a small amt. of H_2SO_4 in a rectifying column which may be operated continuously.

Naphtholsulfonic acids. BRITISH DYE STUFFS CORPORATION, LTD., J. BADDILEY, J. B. PAYMAN and E. G. BAINBRIDGE. Brit. 186,515, Sept. 10, 1921. 1-Naphthol-4-sulfonic acid is obtained by sulfonating α -naphthol with chlorosulfonic acid at a low temp. in an inert solvent preferably C_2H_5Cl ; C_6H_6 or $C_6H_5NO_2$ also may be used. Examples are given of the prepn. of a soln. of the Na salt by directly treating the reaction mixt. with H_2O and $NaCl$, and also by way of the Ca salt.

Synthetic thymol. BADISCHE ANILIN & SODA FABRIK. Brit. 186,202, July 18, 1921. 1-Methyl-4-isopropyl-3-hydroxybenzene and an isomer thereof are prepd. by treating *m*-cresolsulfonic acid with isopropyl alc. and concd. H_2SO_4 or with isopropyl hydrogen sulfate at a raised temp., and subsequently splitting off the sulfonic group by distn. in steam. The oil is freed from isopropyl ether compds., e. g., by treatment with $NaOH$, and the product fractionally distd. From the after-runings is obtained by crystn. from benzene a *thymol isomer*, m. $114-115^\circ$. Thymol can be recrystd. from ligroin.

Reducing solutions with metallic reagents. W. O. MITSCHERLING. U. S. 1,432,775, Oct. 24. Metallic reducing agents such as Zn or Fe are placed in a rapidly rotating tube through which $PhNO_2$ or naphthalenenitrotrisulfonic acid or other soln. to be reduced is passed under the influence of centrifugal force which serves to insure contact with the finely divided reducing metal.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

Nature and origin of diastatic enzymes. E. ROTHLIN. *Münch. med. Wochschr.* 69, 88-9(1922); cf. *C. A.* 16, 3908.—Polemic with Biedermann and remarks of Biedermann in answer. S. AMBERG

Proteins. III. The colloid chemistry of the proteins. A. FODOR. *Kolloid Z.* 30, 313-36(1922).—Impossible to abstract except at great length. Some of the points considered are: (1) mention of the recent workers who have developed the physical-chem. view of protein equilibria; (2) consideration of protein solns. under the usual laws for dil. solns. of electrolytes; (3) reversible gel-sol systems of albumin, globulin, fibrin and phosphoproteins; (4) "micellar" and surface-adsorbed water; (5) further extension of 3; (6) combination with alkalies, acids and salts; (7) the swelling of acid and alkali protein; (8, 9, 10, and 11) the water-equil.-relations, and alteration in phys. properties by acids, alkalies, and salts; (12) effect of H^+ and OH^- on enzyme action upon proteins. H. W. BANKS, 3rd.

Sensitivity of cells to poisons, as a function of their colloidal state. H. HANDOVSKY. *Kolloid Z.* 30, 336-41(1922).—Two factors are considered: (1) The toxicity of the poison and (2) the resistance of the cell. H. terms the inverse of the latter, sensitivity. The effect of colloidal state on each of these factors is shown by the effect of NaCl upon hemolysis by saponin. The effect of other salts was also studied. H. W. B., 3rd.

Colloidal-chemical characteristics of separate fractions of serum protein. J. REITSCHÖTTER. *Oesterr. Chem.-Ztg.* 25, 29-34(1922).—This deals principally with the protective action of the various fractions of different sera, expressed as Zsigmondy's gold number. Sera from a number of animals, both normal and diseased, preps. of antitoxins, etc., were found in most cases to give characteristic gold numbers. The pathol. condition of the individual influences this largely, as does the relative proportion of albumin : globulin : paraglobulin, etc. Similar expts. with various electrolytes were also made with $Fe(OH)_3$ sol. The relative protective action of the different fractions is altered with the acidity of the medium. H. W. BANKS, 3rd.

Lactic acid fermentation of glucose by peptone. G. SCHLATTER. *Biochem. Z.* 131, 362-81(1922).—A retesting of the work of E. Bauer and E. Herzfeld on fermentation without yeast (*C. A.* 15, 3852). S. found that glucose is quantitatively changed to lactic acid by peptone at 37° in solns. which contain $NaHCO_3$ as a buffer. The end of the fermentation is reached when the peptone flocculates. The velocity, or rather the duration of the fermentation, depends upon the concn. of the reacting constituents and takes place more rapidly the more peptone is present while the sugar concn. has only a small influence. Phosphate apparently plays an important role since phosphate-free peptone is unable to stimulate a glucose-lactic acid fermentation. If the peptone-glucose soln. is heated before the addition of the buffer the fermentation power is not destroyed. Only during fermentation does the number of free amino groups of the peptone increase. Control tests failed to show any lactic acid bacteria present. F. S. HAMMETT

The inactivation of saccharase by iodine. H. v. EULER AND S. LANDERGRÉN. *Biochem. Z.* 131, 386-9(1922).—A soln. contg. 0.74 mg. I_2 and 1.5 mg. KI per cc. was mixed in definite proportions with saccharase soln. and held at 17° for 1 hr. The mixt. was then added to a sucrose soln. contg. 4.8 g. of sucrose and 2% PO_4 . The total vol. was 60 cc. Control tests showed that KI in the concn. used (0.01 N) did not exert an

inactivating effect on the enzyme. The relative inversion velocity in one expt. was 58.7% when 0.07 mg. I_2 was present and 45.9% with 0.74 mg., a very narrow range of decrease as compared with the range of inhibiting substance. An attempt to reactivate the saccharase by treatment of the mixt. with $Na_2S_2O_3$ was unsuccessful. The sensitivity of saccharase towards I_2 is marked but the fact remains that a part of the activity is quite resistant and functionable even in relatively concd. solns. of I_2 .

F. S. HAMMETT

Chemistry of the lungs. II. A new phosphosulfatide in the lungs. U. SAMMARTINO. *Biochem. Z.* 131, 411-2(1922).—Six kg. of fresh lung tissue were dried in vacuum on Ag plates. The 1080 g. residue was extd. with benzine and then with boiling alc. The white ppt. which came out on cooling was removed and there was added to it the additional ppt. produced on refrigeration of the ext. The alc. ext. was concd. in vacuum and taken up with Et_2O . The Et_2O soln. was dried with $MgSO_4$, concd. and taken up with alc. for the later sepn. of cephalin. The soln. was freed from a small ppt. with ammoniacal Pb acetate soln. and the filtrate freed from Pb and NH_4 with H_2SO_4 . The filtrate was concd. in vacuum and pptd. with acetone. The white substance obtained was sepd. into an inorg. and an org. fraction with boiling alc. On cooling the org. compd. crystd. out. All fractions gave the same m. p. (197°). The relation of N : P : S was 2 : 1 : 1, resp. No orcinol reaction was given. Pb was absent. The compd. was neutral to litmus. Elementary analysis gave: 62.98 C, 12.36 H, 2.83 N, 3.23 S, 3.12 P, and 15.48% O, in close agreement with the calcd. for $C_{39}H_{72}N_2S_2P_2O_{13}$. S. considers the compd. the anhydride of a phosphosulfatide. F. S. H.

The abietret protein nitrogen of milk, cow and human. A. MADER. *Klin. Wochschr.* 1, 1555-7(1922).—The abietret constituents of milk were obtained either by dialysis or by ultrafiltration. The amino acid concn. of the dialyzate or ultrafiltrate was then detd. with the ninhydrin reaction, the quant. procedure of Riffart being used. Cow milk contains 18-21, human milk 51-60 mg. of abietret amino-acid N per l. M. H.

Properties of dibenzoylcystine. C. G. L. WOLF AND E. K. RIDEAL. *Biochem. J.* 16, 548-55(1922).—Benzoylcystine is, according to Gortner and Hoffmann (*C. A.* 16, 517), the simplest known type of organic substance which exhibits gelation with water, hence W. and R. have selected it to study some of the elementary properties of gels. Gels of dibenzoylcystine are prepared by peptization with hot water. The substance is quite a strong acid with a dissociation const. of 1.49×10^{-3} . The gel structure appears to be fibrillary and relatively coarse. The Na salt of the acid shows no gelatinizing power. The presence of acids reduces the soly. of the substance. NH_4 -CNS reduces the water-retaining power of the gel. Cationic dyes are adsorbed and pptd. by the gel. Anionic dyes diffuse in a normal manner, while halogen dyes apparently react chemically with the S group. Di-*m*-nitrobenzoylcystine has properties similar to the simpler compd. A possible structure of the gel fibril based upon the effect of chem. substitution on the gel formation is suggested. B. H.

Nitrogen distribution in Bence-Jones protein, with a note upon a new colorimetric method for tryptophan estimation in protein. ERY LÜSCHER. *Biochem. J.* 16, 556-63 (1922).—The N distribution was detd. by the Van Slyke method. Between the Bence-Jones protein and serum globulin, the main difference lies in the non-amino N of the filtrate. The tissue proteins, on the other hand, contain larger amts. of diamino acids. A modification of the Fürth method for the estn. of tryptophan is proposed.

BENJAMIN HARROW

The two forms of gelatin and their isoelectric points. J. A. WILSON AND E. J. KERN. *J. Am. Chem. Soc.* 44, 2633-6(1922).—Working at 7°, it was found that gelatin, like collagen, shows 2 points of min. swelling with change of H ion concn., at pH 4.7 and 7.7. It is suggested that they represent the isoelec. points of the gel and sol forms of gelatin, resp. C. A. R.

Action of amino acid in protecting amylase from inactivation by mercury. H. C. SHERMAN AND MARY L. CALDWELL. *J. Am. Chem. Soc.* **44**, 2923-6(1922); cf. *C. A.* **16**, 572.—Gortner having suggested that the failure of histidine and tryptophan to show a favorable influence, like other NH_2 acids, upon the amylolytic action of purified pancreatic amylase might have been due to the presence of traces of Hg, inasmuch as pptn. by Hg is used as a step in the prepn. of the 2 compds.; expts. have been carried out in the same manner as those previously reported for the 2 substances but with glycine and phenylalanine with and without HgCl_2 added to the starch paste substrate before digestion with amylase. It was found that these two, and therefore presumably other, NH_2 acids protect against small concns. ($0.000006\text{ }M$) of HgCl_2 in testing the amylolytic and saccharogenic action of purified pancreatic amylase and allow the latter to act almost as efficiently as if no Hg were present. Since there is a decided increase in the activity of the amylase in the presence of the two NH_2 acids even when HgCl_2 has been added, it seems certain that such minute amts. of Hg as might conceivably have been present in the histidine and tryptophan preps. used in the earlier work could not account for their entire lack of activating influence on the amylolytic action of the enzyme. C. A. R.

Influence of lysine upon the hydrolysis of starch by purified pancreatic amylase. H. C. SHERMAN AND MARY L. CALDWELL. *J. Am. Chem. Soc.* **44**, 2926-30(1922); cf. preceding abstr.—Lysine, unlike glycine, has no apparent favorable influence on the amylolytic activity of the amylase, but, like glycine, it consistently has a favorable effect on the saccharogenic action. According to the view that the enzyme is essentially at protein substance which gradually becomes inactivated through hydrolysis in the aq. medium in which it acts and that the apparent "activating" action of NH_2 acids is due to retardation of this hydrolysis, it appears probable that the lysine in the enzyme mol. is so bound that it would not in any case be split off until after the stage of amylolytic action had been passed but that it is concerned in the later stages represented by saccharogenic activity, and that therefore the addn. of lysine tends to conserve the enzyme by diminishing the rate of its further hydrolysis at this later stage. C. A. R.

Influence of some organic compounds upon the hydrolysis of starch by salivary and pancreatic amylases. H. C. SHERMAN AND NELLIE M. NAYLOR. *J. Am. Chem. Soc.* **44**, 2957-66(1922).—The favorable effect reported by Rockwood (*C. A.* **12**, 486) to be exerted by several types of org. compds. upon the activity of amylolytic enzymes, in consequence of which he designated such compds. as auxo-amylases, appears to have been due in most, if not all, cases, other than those of natural NH_2 acids, to H ion or salt effects rather than to the org. structure of the compds. In the presence of favorable concns. of Cl , PO_4 and H ions, MeNH_2HCl , EtNH_2HCl , $\text{PhNH}_2\text{H}_2\text{SO}_4$, BzOH , BzNH_2 , $\text{H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ and $\text{BzNHCH}_2\text{CO}_2\text{H}$ showed no favorable effect upon the activity of salivary or pancreatic amylase. Previous findings regarding the favorable influence of several NH_2 acids resulting from protein hydrolysis have been confirmed and extended. This influence may be attributed either to a direct "activating" effect dependent upon the structural nature of these substances as $\alpha\text{-NH}_2$ acids or to conservation of the enzyme by retarding its hydrolysis. Although the first hypothesis is not disproved the results with hippuric acid fail to support it and all the results obtained in this work can be explained on the basis of the second hypothesis alone. C. A. R.

B—METHODS AND APPARATUS

STANLEY R. BARNEDICT

Demonstration of hemochromogen crystals by the method of Takayama. G. STRASSMANN. *Munch. med. Wochschr.* **69**, 116-7(1922).—Three parts each of 10% NaOH, pyridine and glucose are mixed with 7 parts distd. water. Several drops are

added to a particle of blood when, after some min., hemochromogen crystals are formed which keep well in this mixt.

S. AMBERG

The nature of the mastix reaction with cerebrospinal fluid. Preliminary notice. E. SAHLGRÉN. *Münch. med. Wochschr.* 69, 618-9(1922).—Normal cerebrospinal fluid was treated with 9 times its vol. of alc. The ppt. was centrifuged, washed several times with alc., and taken up in saline soln. It did not show any protective action or very little when tested with mastix soln. The alc. was evapd. The residue, taken up and tested, gave the same protection as the original fluids. On dialysis the protective substance goes into the dialyzate. Normal cerebrospinal fluid evapd. in a beaker, intensely heated, and with water added to original vol., behaved like original fluid. Pathol. fluids treated in the same manner gave the same results as normal fluids. The protective action of normal fluids depends on the p_H of the fluid. Various protein fractions were pptd. from blood by means of $(NH_4)_2SO_4$. The different fractions were dialyzed, NaCl and phosphate mixt. added to the proper p_H and tested with mastix soln. The different protein fractions showed different results. Fibrinogen gave the strongest flocking out, and albumin none at all. For the mastix curve in pathol. cases there enter into consideration the p_H of the fluid, the total amt. of globulins (and possibly of albumin as the latter may influence the globulin curve) and the quant. relationship of the various globulin fractions.

S. AMBERG

The determination of total nitrogen of urine and the residual nitrogen of blood without distillation and titration. W. AUTENRIETH AND H. TAEGER. *Münch. med. Wochschr.* 69, 1141-3(1922).—The method is based on a Kjeldahl digestion with CaO_2 as catalyst and subsequent nesslerization.

S. AMBERG

A method for the preparation of cystine. C. L. A. SCHMIDT. *Proc. Soc. Exptl. Biol. Med.* 19, 50-2(1921).—Human hair or wool, from which the oil has been extd. with gasoline, is heated at 100° with twice its wt. of concd. HCl. Hydrolysis of the protein is usually complete in 12 hrs.; heating is discontinued when the biuret test becomes feebly positive or negative. Vacuum distn. at $60-70^\circ$ removes the greater part of the HCl, and the vol. is restored by the addn. of H_2O . A thick aq. suspension of com. finishing lime is slowly added, a high temp., being avoided until the mixt. becomes chocolate-colored. It is then filtered and the residue washed with distd. H_2O . The clear, brown filtrate is partially neutralized with HCl, and the acidity brought to p_H 4-5 with AcOH. On standing overnight in the ice chest, crude cystine sediments. Purification is effected by dissolving in a minimum amt. of 5% HCl; decolorizing by boiling for several mins. with charcoal which has been previously boiled with HCl to remove the $Ca_3(PO_4)_3$; neutralizing the hot soln. with Na acetate until a drop turns Congo red paper blue; crystn. of cystine takes place in the cold. The crystals are freed from tyrosine by repeatedly washing with hot H_2O . The yield is about 6.3%.

C. V. B.

A micro-Winkler method for the quantitative determination of dissolved oxygen. E. J. LUND. *Proc. Soc. Exptl. Biol. Med.* 19, 63-4(1921).—Winkler's method is applied to 10 cc. or even 5 cc. of water in the following way. $MnCl_2$ soln. 0.10 cc., and NaOH-KI soln. 0.10 cc. are added to the sample. The thiosulfate soln. is dild. to $1/10$ its usual concn. The I is titrated in a tall dish, a 5 cc. buret being used. The end point is as definite and the error the same as in the ordinary procedure. The small vol. permits of rapid temp. adjustment. The rapidity of the test makes it applicable to the study of O consumption by protozoa, eggs and certain kinds of tissues. The max. error is less than 0.005 cc. of O_2 .

C. V. B.

The sensitivity and reciprocal action of blood catalyst and organic and inorganic catalysts. ANGELO BELLUSSI. *Arch. farm. sper.* 34, 6-16, 29-32, 37-48(1922).—The peroxidase test with PhOH and H_2O_2 is by no means specific for blood. The same

rose color is produced by very dil. solns. of Cu and Fe^{++} salts and $\text{K}_4\text{Fe}(\text{CN})_6$ and by concd. solns. of NaCl, CaCl_2 , KCl and MnCl_2 . No color was obtained with salts of Pb, Sn, Hg, Ag, Sb, Zn, Co, or bromides, iodides, chromates or CrO_2 ; juice of garlic, carrot, turnip, tomato, onion, potato, spinach, beet; saliva, milk, nasal mucus, sperma. CuSO_4 was active at a dilution of 1 : 200000 and FeSO_4 at 1 : 20000. Colloidal Cu was very active. Mixtures of blood with dil. CuSO_4 , FeSO_4 and $\text{K}_4\text{Fe}(\text{CN})_6$, resp., gave reactions more intense than the sum of the separate reactions. At dilutions where the separate catalysts gave no reaction, the mixtures reacted almost immediately. In contrast to the accelerating effect of Cu and Fe on the blood catalyst, chlorides of Mn, Na, K and Ca had a retarding effect. Blood appears to be specific in its sensitivity to this retardation, since these chlorides accelerate the action of each other and of Cu and Fe.

A. W. DOX

Detection of blood. P. N. VAN ECK. *Pharm. Weekblad* 59, 1098-1100(1922).—The constituent of blood which is responsible for the color reaction with benzidine and H_2O_2 is very stable. Both the tar and the residue obtained by destructive distn. of blood give, in AcOH soln., a strong benzidine reaction. It cannot be assumed that the original substance is volatile, but rather that a volatile decompn. product still contains the grouping to which the reaction is due. It is not probable that blood is the only material whose distn. products give this reaction. However, negative results were obtained with egg albumin, feathers, hair and leather. Ten specimens of feces contg. blood gave a positive reaction, while with 10 specimens free from blood the test was negative. The tar from anthracite, bituminous coal, wood and peat gave no reaction with benzidine unless the substance was mixed, previous to distn., with dried blood. Pending further investigation the above test may be of value in the identification of blood, but should not be relied upon exclusively.

A. W. DOX

Micromethod for the determination of ethyl alcohol in blood. E. M. P. WINKMARK. *Biochem. Z.* 131, 473-84(1922).—A 50 cc. Erlenmeyer flask is fitted with a well ground glass stopper. The exterior part of the stopper is drawn out and bent into a hook: the part of the stopper within the flask is drawn out and formed into a small cup-like container which holds about 0.2 cc. and when the stopper is in place is about 1 cm. from the bottom of the flask. A drop of blood is obtained by finger puncture, taken up in the capillary pipet, weighed, blown into the cup and the empty capillary weighed. The cup-bearing stopper of the Erlenmeyer is now fitted to the flask into which has been carefully measured 1 cc. $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ soln. This mixt. is prepd. by weighing 0.250 g. c. p. recrystd. $\text{K}_2\text{Cr}_2\text{O}_7$ into 1 cc. of H_2O and quant. transferring the soln. into a 100 cc. vol. flask with concd. c. p. H_2SO_4 and filling to the mark with the same. Such a soln. is used for amts. of alc. around 0.5%. For amts. around 0.1% 0.05 g. $\text{K}_2\text{Cr}_2\text{O}_7$ is used. The flask with appropriate controls is covered with a rubber cap and placed in a water bath at $50\text{-}60^\circ$ for 2 hrs. ± 15 min. The alc. distd. over into the $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ mixt.; 25 cc. of distd. H_2O is added and 0.5 cc. of a 5% iodate-free KI soln. After from one half to a minute the mixt. is titrated with 0.01 N or 0.005 N $\text{Na}_2\text{S}_2\text{O}_3$ soln. with a 1% starch soln. as indicator. The indicator is added towards the end of the titration. The blue color reappears. The difference between the controls and the blood test is proportional to the amt. of alc. The difference between the 2 readings, times 1.15 gives the alc. amt. when 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ is used. When the 0.005 N is used the factor is 0.57. The errors in the method are of such an order that the analytical results should not be expressed in more than 2 significant figures. The weak point in the method is the $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ mixt.

F. S. HAMMETT

A reaction of urea with *p*-dimethylaminobenzaldehyde. I. H. K. BARRENSCHIEEN AND O. WELTMANN. *Biochem. Z.* 131, 591-5(1922).—Neither uric acid, the purine bases and their derivs., guanidine and the guanidine derivs., creatine and crea-

tinine, a series of amino acids, carhamic acid salts, or NH_4 salts give the Ehrlich reaction as does urea. Allantoin, however, is an exception. If 10 cc. of a 0.01 mol. urea is dild. in arithmetical progression in differences of 0.5 cc. it is found that a positive reaction is given in the 19th member of the series or a dild. of 0.001 mol. In a dild. of 0.0005 mol. the test is not given. Normal urine which has been dild. 200 to 1000 times still gives the reaction. In blood serum which has been deproteinized by $\text{CCl}_4\text{CO}_2\text{H}$ the sensitivity is less than in pure urea solns. The reaction with pure urea is also given in alc. soln. The presence of free H-ions is essential, although the source is a matter of no particular importance. The addn. of 40% HCHO in excess does not inhibit the reaction. Alkali disturbs the formation of the color. In the practical application of the test 1 cc. of filtrate, representing 0.5 cc. serum, is mixed with 2 drops of the reagent. In all cases where the rest N is over 36 to 40 mg. the reaction is positive. P. S. H.

The determination of the actual reaction of tissues by thread indicators. A method for the diagnosis of death. SILVIO REBELLO. *Arch. intern. pharmacodynamie* 26, 395-405(1922).—Threads stained with alc. and alk. solns., resp., of bromothymol blue are passed by means of a needle through a fold of skin and left for 1 hr., at the end of which time the threads are withdrawn, and a change of color in the indicator towards the acid side (yellow) is taken by R. as conclusive evidence of death. The method is extended by choosing appropriate indicators to cover the range of H-ion variations of various tissues. W. A. PERLZWEIG

Specific precipitin reaction of leucocytes. LUDWIG HEKTOEN AND F. R. MENNER. *J. Am. Med. Assoc.* 79, 1328(1922).—Exts. of dog and of guinea pig leucocytes were obtained by the injection of a suspension of wheat gluten in the pleural or peritoneal cavity. The leucocytes were thoroughly washed in salt solu. and definite amts. by wt. were suspended in water and well shaken. An equal vol. of physiol. NaCl solu. of double strength was added and the suspension dild. to 1 of leucocytes to 10, 20 or 100 of total vol. Rabbits were injected intravenously at 3-day intervals with increasing amts. of such exts., say 2, 3, 4, 5, and 6 cc. of a 1 to 20 solu. The serum was tested about the 5th day after the last injection. The results show that "the precipitin for dog serum in the antiserum for dog leucocytes may be removed by means of specific absorption. Exts. of dog leucocytes obtained by fractional centrifugation of citrated dog blood gave similar results as exts. of leucocytes in exudate. Expts. of the same general nature with exts. of the leucocytes in human blood showed that the precipitin for homologous serum may be removed from the antiserum by mixing it with dild. human serum without any apparent reduction in the precipitin for leucocytic ext. Leucocytes appear to contain specific elements not found in red corpuscles, platelets or blood serum, and these elements may be present in the serum of inflammatory exudates. L. W. RIGGS

Comparative values of indigo carmine and blood biochemical tests in the estimation of kidney function. B. A. THOMAS. *J. Am. Med. Assoc.* 79, 1387-9(1922).—Figures are given for 12 normal and for 15 pathologic cases. Analysis of the figures shows that indigo carmine as employed has proved itself eminently reliable as a gage of kidney function; also that the 3 blood chemistry tests likewise have proved their reliability; that of these, if there be any choice, urea N is probably the most practical and best; that, if a supplementary or confirmatory test to indigo carmine or one of the elimination tests is indicated, a blood chem. test, notably the urea N should be employed; that both tests of elimination and retention are indispensable for the proper conduct of the work, and that if the values for indigo carmine are found to be normal, any other test is superfluous. L. W. RIGGS

Normal hemoglobin standard. R. L. HADEN. *J. Am. Med. Assoc.* 79, 1496-7 (1922).—A study of the normal hemoglobin value in 52 persons led to the following recommendations. All hemoglobinometers should be calibrated in terms of a uniform

standard. The ferricyanide method as adapted by Van Slyke affords the most desirable means of standardization. The ideal standard takes as 100% the av. normal number of g. of hemoglobin per 100 cc. for each 5 million red cells. On this basis with the Van Slyke app. the hemoglobin in 52 normal persons was 15.6 g. per 100 cc. for each 5 million red cells. All hemoglobinometers should be calibrated to this standard.

L. W. RIGGS

The isolation of histidine from blood. S. DEMJANOWSKI. *Z. physiol. Chem.* **122**, 93-7(1922).—Defibrinated blood is hydrolyzed by heating with 0.5 its vol. of HCl of sp. gr. 1.19 in an autoclave at 1.5 atm. for 6 hrs. or at ordinary pressure for 10 hrs. Solid Na_2CO_3 is then added until the soln. is just acid to litmus. After standing 24 hrs. the ppt. is filtered, the yellow filtrate made alk. with hot, satd. Na_2CO_3 soln. and heated until all the NH_3 is expelled. A ppt. forms which is filtered and after diln. of the filtrate hot, satd. HgCl_2 soln. is added until there is no further pptn. The reaction should remain alk. This ppt. is allowed to stand 24 hrs. It is then filtered and rubbed thoroughly in a mortar with the minimal quantity of 10-15% HCl necessary to produce acidity to Congo red paper. A portion of the ppt. remains undissolved and is removed by filtration. The filtrate is made alk. with hot satd. Na_2CO_3 and, if necessary, a small quantity of hot, satd. HgCl_2 soln. is added. A gelatinous ppt. forms, the amt. of which is increased by diln. with H_2O . It is sepd. by filtration and decomposed repeatedly with H_2S . The filtrate from the HgS is evapd. to $\frac{1}{3}$ its vol. and if the odor of HCl is not perceptible concd. HCl is added. The dihydrochloride of histidine ppts.; the yield is 90 g. crude product from 8.5 l. blood.

R. L. STEHLÉ

C—BACTERIOLOGY

A. K. BALLS

The activation of cell functions by measures which increase the activity. W. WEICH-ART. *Deut. med. Wochschr.* **47**, 885-6(1921).—Water-sol. substances from alc. exts. of guinea pig tissues added to standard media favor the multiplication of bacteria such as hemolytic and other streptococci. There is an optimum of such additions.

S. AMBERG

Increase of virulence of apathogenic bacteria by chemical means. B. LANGE AND M. YOSHIOKA. *Deut. med. Wochschr.* **47**, 1322-3(1921).—Much reported that some apathogenic bacteria became pathogenic when injected together with lactic acid. This paper reports similar expts. Of special interest is the result obtained with *B. proteus* which had been killed by heat; the simultaneous injection of bacilli and a certain amt. of 2% lactic acid killed while lesser concns. did not. Similar results were obtained with living bacilli. In some expts. the virulence of proteus grown on lactic acid agar was increased. The conclusion is that it was not possible to render apathogenic bacteria (air sarcinas, *B. subtilis*) virulent by simultaneous injections with lactic acid. The pathogenic activity of proteus (living and dead) can be increased by simultaneous injection of acid when the dose of the acid is not too far removed from the fatal dose. This cannot be explained by an increase in the virulence of the bacilli. The observations with the addn. of lactic acid to the medium do not exceed variations of virulence which have been frequently seen in bacteria grown on various media.

S. A.

Comparison of the methods for testing and comparing the value of disinfectants. E. HAILER. *Deut. med. Wochschr.* **47**, 1384-7(1921).—Tests for the bactericidal power of disinfectants and their comparison can only be accomplished properly by the use of germ carriers.

S. AMBERG

The bacterial content of the stomach as influenced by saliva. NICHOLAS KOPELOFF. *Proc. Soc. Exptl. Biol. Med.* **19**, 110(1921).—Fractional samples of human gastric contents were obtained at intervals of 15 mins. by the Rehfuß method. A second series

of samples was obtained while the subject's saliva was drained from the mouth by a dental suction tube. The bacterial content of the 1st series was enormously in excess of the 2nd, and seemed to be entirely dependent upon the amount of saliva swallowed, and not related to the acidity or the digestive phase. Qualitatively, the bacteria of the saliva and samples were the same. Bacteria in samples obtained by the Rehfuess method cannot be indicative of a gastric lesion. C. V. B.

The effect of the accessory substances of plant tissue upon growth of bacteria. O. T. AVERY AND H. J. MORGAN. *Proc. Soc. Exptl. Biol. Med.* 19, 113(1921).—The addition to media of fresh plant tissue such as white and sweet potato, yellow and white turnip, banana, carrot, beet or parsnip, supplies the necessary factors for growth of hemoglobinophilic bacilli, and favors the growth of organisms whose multiplication is otherwise greatly restricted by a narrow zone of p_H . The presence of the plant tissue permits the aerobic growth of certain bacteria which ordinarily fail to grow in the presence of O_2 . The studies suggest the presence of certain oxidizing and reducing enzymes in fresh plant tissue as well as the so-called accessory food substances. C. V. B.

Collodion sacs for aerobic and anaerobic bacterial cultivation. F. L. GATES. *Proc. Soc. Exptl. Biol. Med.* 19, 121(1921).—Collodion sacs of 5–10 cc. are formed in test-tubes lined with a dried film of gelatin (the 10% gelatin soln. contains 0.3% tricresol). Warm water dissolves the gelatin and the sac is readily removed. It is then fitted to a supporting glass tube and inserted into one limb of a V-shaped tube to which the supporting tube is sealed with a collar of rubber tubing. Sac and V-tube are partly filled with water, plugged with cotton, and autoclaved. The chosen medium is placed within the sac, nutritive and growth promoting substances dialyze and the dialyzate is accessible for inoculation through the other limb of the V-tube. For anaerobic culture, vaseline is layered over medium and dialyzate. The method is especially useful with the Smith-Noguchi fresh tissue medium, the organisms being obtained free from the confusing antigenic protein ppt. which develops in this medium. C. V. B.

The agglutinating power of the blood in the snail during hibernation. X. CHAHOVICH. *Compt. rend. soc. biol.* 84, 731–2(1921); *Abstracts Bacteriology* 5, 280.—During hibernation the blood of snails was able to agglutinate *B. coli* and *B. pyocyaneus* in low dilns. (1 : 10 after 3 hrs.). Inoculation of the snails did not increase the agglutinin titer. H. G.

The precipitating power of the blood of the snail during hibernation. X. CHAHOVICH. *Compt. rend. soc. biol.* 84, 987–8(1921); *Abstracts Bacteriology* 5, 280.—Normal precipitins for culture filtrates of *B. coli* or *B. pyocyaneus*, or for dog serum, are not present in the blood of the snail, nor can they be induced by injections given during hibernation. H. G.

The decomposition of citric acid of cow milk by bacteria. H. KICKINGER. *Biochem. Z.* 132, 210–19(1922).—The citric acid content of pasteurized or cooked milk immediately after the procedure is the same as that of the fresh milk. However, after the milk has stood for some time the concn. is less. When milk is fractionally sterilized there takes place at first a rather significant decrease in citric acid concn. After the 3rd sterilization the amt. remains const. Expts. showed that bacteria of the peptonizing group (*B. subtilis*, *B. mesentericus vulgaris* and *Proteus vulgaris*) produce this change in milk while the lactic acid formers, of which 3 different strains were used as well as Joghurt bacilli, had no destructive effect. Some indications were obtained of an enantibiotic action of the lactic-acid-forming-bacteria towards the peptonizing organisms. F. S. HAMMETT

The oligodynamics of silver. IV. R. DOERR AND W. BERGER. *Biochem. Z.* 131, 351–61(1922).—When a 1% KCN soln. is added in pptg. amts. to an oligodynamic soln.

of Ag, the previous power of the latter to kill microorganisms is lost. This effect is attributable to the formation of inactive $\text{Ag}(\text{CN})_2$ ions from the toxic Ag ions. From this it appears that the active principle of the various types of oligodynamic studies with Ag is the Ag ion. The diffusibility and dialyzability of the toxic agent are in agreement with the idea. Moreover, when flasks made of Ag are treated with KCN soln. they lose the power of killing microorganisms in suspension contained therein. The bactericidal power of these flasks is caused by the action of the atm. O and CO_2 on the metal. The attempts made to det. the bactericidal strength of pure colloidal solns. of Ag (without Ag ion) were unsatisfactory and indefinite. F. S. HAMMETT

Bacterial fermentation. F. MÜLLER. *Biochem. Z.* 131, 485-98(1922).—The expts. reported indicate that the influence of peptone as a representative of a protein compd. on the fermentation of sucrose by *B. lact. aerogenes*, and apparently by other bacteria of the coli group, is due to its properties as a N carrier and as a buffer. A 1% peptone soln. is sufficient for the N. More peptone stimulates fermentation by virtue of its buffer action which is similarly obtained by phosphate or citrate mixts. The principle is the same for other protein compds. when their physiol. chem. properties are considered. The course of fermentation of a peptone-sucrose-*B. lact. aerogenes* mixt. is particularly less influenced by the hydron concn. but markedly by the sp. nature of the acids formed which act harmfully only when undissociated. The significance of the sugar concn. for fermentation is in a narrow relationship with the buffer capacity of the nutrient medium. If this is relatively low with respect to the sugar concn. an increase of the latter of over 5% does not accelerate fermentation. If, on the other hand, it is relatively high, an alkalinization succeeds the initial rise in acidity. F. S. HAMMETT

The chemistry of the black coloration of nutrient media containing carbohydrate by *Bacillus mesentericus* var. *niger*. A. MUSCHEL. *Biochem. Z.* 131, 570-90(1922).—*B. mesentericus* var. *niger* grows on nutrient agar in which there is no carbohydrate, polyvalent alcs., or amino acids which are C_6H_5 derivs., without discoloration of the medium: but in media which contain dextrose, galactose, levulose, lactobiose, sucrose, glycerol, dulcitol, or tyrosine the growth of the organism is followed by a darkening of the substrate. By the use of protein-free media it was shown that the discoloration is due to compds. of the benzene series, closely related to the dihydroxybenzenes (*o*- and *p*-) and which apparently form condensation products with the amino acids. This may explain the discoloration effect of the amino acids and the amines when acting together with pyrocatechol and hydroquinone, leading perhaps to derivs. of pseudo indoxyl. F. S. HAMMETT

The d'Herelle phenomenon. R. OTTO, H. MUNTER AND W. F. WINKLER. *Z. Hyg. Infektionskrankh.* 96, 118-60(1922).—The observation of d'Herelle (*Compt. rend. soc. biol.* 1918-1921) that filtrates from stools and broth cultures are bacteriolytic are confirmed. The process is called *bacteriophagy*. Some of the preps. are sp., being limited in their action to organisms from whose cultures they were obtained, while others are nonsp. in that they are bacteriolytic for several species of bacteria. The bactericidal substance is capable of growth. It retains its action unchanged for long periods of time. The bacteriophages act *in vivo* as well as *in vitro* but gave no therapeutic results in man. An antiserum to these bactericidal substances can be obtained. JULIAN H. LEWIS

D—BOTANY

B. M. DUGGAR

The action of saponin substances on plant cells. II. F. BOAS. *Ber. botan. Ges.* 40, 249-53(1922); cf. *C. A.* 16, 3325.—Saponin from different sources was tested.

Cyclamine and digitonin in weak concn. increased the fermentation of sugar by yeast as detd. by the CO_2 output. In strong concn. they prevented fermentation. The action of these 2 substances depends on a chem. combination with the cholesterol of the cell. The lipoids, which are absorbed both on the surface and within the plasma, constitute the most active and important constituents of the cells according to the saponin expts. No parallelism exists between surface activity and the action of the saponin substances.

F. C. Cook

The presence of aucubin and sucrose in the seeds of *Rhinanthus crista-galli*. M. BRIDEL AND M. BRAECKE. *Compt. rend.* **175**, 532-4(1922).—The glucoside aucubin was isolated by extrn. with acetone and identified after hydrolysis using (1) H_2SO_4 , and (2) emulsin. Sucrose was isolated as a Ba salt from EtOH. The Ba was removed with dil. H_2SO_4 and the soln. filtered and taken to dryness under reduced pressure. The residue was twice extd. with EtOH from which the sucrose crystd.

F. C. C.

Rhinanthin and aucubin—Rhinanthin is obtained from impure aucubin. M. BRIDEL AND M. BRAECKE. *Compt. rend.* **175**, 640-3(1922).—The product extd. by Ludwig in 1870 from *Rhinanthus crista-galli* and called rhinanthin is not a pure product but a mixt. of sucrose and aucubin in variable proportions. The name does not designate a definite chem. substance and should be dropped.

F. C. C.

The relation existing between the relative acidity of the tissues and the presence of anthocyanin in the outer coating of lily bulbs exposed to light. M. MIRANDÉ. *Compt. rend.* **175**, 711-13(1922).—A general acidification due to the wound and to an acidity related to pigmentation is produced in the outer coating of the lily bulb when sepd. and exposed to light. The relation of oxidase to these acidity changes, which are apparently oxidation changes, is discussed. The phenomena of oxidation take part in the synthesis of anthocyanin.

F. C. Cook

The influence of sucrose on green etiolated cotyledons isolated at various stages of germination. FRÉ. S. MANSKY. *Biochem. Z.* **132**, 18-25(1922).—Expts. with germinating gourd seeds showed definitely that the stage of development is a significant factor in the need of sucrose for the formation of chlorophyll, and general growth of the etiolated cotyledons. The young structures (11 days) become green in H_2O culture in the light and are uninfluenced by weak sucrose solns.; strong solns. of the carbohydrate retard chlorophyllation. The formation of chlorophyll is connected with the formation of dry matter, decreasing in such seed leaves as the latter increases. The retardation of growth in 20% sucrose solns. is probably related to the retardation of chlorophyll formation. The older etiolated cotyledons (18 days) form very little chlorophyll in the light in H_2O culture unless sucrose is present. At this stage growth is also favored by sucrose. A concn. of 5% is the best. 20% acts as an inhibiting agent here as at the younger stage. The addition of $\text{Na}_2\text{S}_2\text{O}_4$ inhibits the storing of chlorophyll in the structures studied. In later stages (31 days) sucrose favors the storage of foodstuffs in the plants as detd. by the increase in dry matter. The chlorophyllation in the light in sucrose-contg. solns. is slow. The results as a whole indicate the complexity of the factors in the "greening" process, such as, incompletely formed plastids; retarded initial growth; a beginning destruction of plastids in the later stages of development; and lack of necessary carbohydrate. Sucrose, then, is essential if it relieves the latter deficiency, harmful if it retards growth, and of no significance if the cells can draw on their own supply.

F. S. HAMMETT

Hippuric acid and urea as foodstuffs for plants. TH. BOXORNY. *Biochem. Z.* **132**, 197-209(1922).—Studies with certain seedlings and yeast demonstrated that hippuric acid is toxic to plants when it has penetrated into the organisms. This is probably due to the splitting off of benzoic acid. At a diln. of 0.09% the harmful effect of hippuric acid is not in evidence while benzoic acid is scarcely, if at all, harmful at a concn.

of 0.05%. This is fair agreement. Urea in a concn. of 1% is not completely harmless, though it does act as a nutrient if NH_3 is not liberated by fermentation. This NH_3 production can be prevented by antiseptics. Urea of itself is a harmless source of N for the plants, and hippuric acid is harmful in too concd. solns. The harmlessness of maturing with urines containing hippuric acid is attributed to the diln. through admixt. with the soil. Moreover the soil organisms may well take it up and oxidize the benzoic acid to CO_2 .

F. S. HAMMERT

The odorous constituents of apples. II. Evidence of the presence of geraniol. F. B. POWER AND V. K. CHESNUT. *J. Am. Chem. Soc.* **44**, 2938-42(1922); cf. *C. A.* **14**, 2829.—An examn. of McIntosh apples, a particularly fragrant variety of the fruit, has confirmed the results of the earlier investigation that the odorous constituents of the apple consist chiefly of Am esters and has given further information respecting the substance which imparts to some apples a distinctly rose-like odor. Although the amt. of this substance, even in the McIntosh apple, is extremely small, it has been possible to det. with a considerable degree of certainty that it consists of geraniol; hydrolysis of the esters of the apple gave a product which had, besides the odor of AmOH, a rose-like fragrance and yielded on oxidation valeric acid and a product having the characteristic odor and other properties of citral; at the same time, the formation of very small amts. of Me_2CO and levulinic acid, the further oxidation products of geraniol or citral, was decisively indicated.

C. A. R.

Confirmation of the occurrence of linalyl esters in peaches. F. B. POWER AND V. K. CHESNUT. *J. Am. Chem. Soc.* **44**, 2966-7(1922).—That the odorous constituents of peaches consist chiefly of esters of linalool (*C. A.* **16**, 53) has been further confirmed by the observation that the oxidation product of the odorous constituents contains, in addn. to the citral already reported, small amts. of Me_2CO and levulinic acid.

C. A. R.

F—NUTRITION

PHILIP B. HAWK

NORMAL

Simple method for administration of iodides in the food in goiterous regions. A. D. HIRSCHFELDER. *J. Am. Med. Assoc.* **79**, 1426-7(1922).—A stock of iodized salt contg. NaCl 99 and KI 1 is made up and kept on hand. As each 5 lb. bag of salt is purchased it is spread in a thin layer and 5 teaspoonfuls of the iodized salt are evenly added to the 5 lbs. by means of an ordinary salt shaker. The salt thus treated is thoroughly mixed and used in cooking and for table salt.

L. W. R.

Faulty diet and its relation to the structure of bone. P. G. SUTLEY. *J. Am. Med. Assoc.* **79**, 1563(1922).—Deficiency diseases in man usually have a complex etiology and the dietary defects which produce them may be caused by few or incomplete protein and improper amts. of carbohydrates and salts along with lack of vitamins. Among the dietetic principles concerned in the growth of bone are (1) an uncharacterized org. substance which is distinct from fat-sol. A. This is found in cod, burbot and shark livers in large amts. and in small amts. in butter and in coconut oil, the latter containing no fat-sol. A. (2) Ca. (3) P. (4) Water-sol. B. (5) Fat-sol. A. Water-sol. C influences the structure of the bone of the guinea pig but the rat either does not need this substance or else is able to synthesize it. Bones of animals whose diet is adequate except for fat-sol. A are perfectly calcified, but a high degree of osteoporosis develops. The same result follows the use of diets having a deficiency only in water-sol. B; there is also an aplasia of the marrow such as follows complete starvation, and later hemorrhage into the medullary cavity. The optimal amt. of Ca which the diet can furnish for growth maintenance and function in the rat is about 0.641 mg. per 100 g. of ration when all other

factors of the diet are satisfactory. The amt. of P has not been detd. so accurately but appears to be about 0.49 mg. per 100 g. of food. Diets contg. 0.832 mg. of Ca and 0.305 of P, or 0.052 of Ca and 0.364 of P per 100 g. of food will produce rickets. A rat fed the first ration has the normal amt. of Ca but only $\frac{1}{2}$ the normal amt. of P in the blood serum, while a rat fed the second ration has the normal amt. of P but only $\frac{1}{2}$ or less of Ca. If the org. substance so abundantly present in fish oils is supplied freely rickets will not develop in spite of a faulty ratio of Ca to P in the food. Animals exposed to direct rays of the sun, or to Fe-Cr, Cd, or Hg-quartz vapor light are enabled to compensate for faulty Ca-P ratios. Apparently the shorter ultra-violet rays (about 2100 Angström units) have the greatest antirachitic effect. The same changes in the blood salts are induced under the influence of these rays as by cod liver oil. L. W. R.

Decalcification of teeth and bones, and regeneration of bone through diet. P. R. HOWE. *J. Am. Med. Assoc.* 79, 1565-7(1922).—From a point near the enamel border of a tooth a cross section about 1 mm. in thickness was taken, the cementum and pulp were removed, the section was washed, dried at 100° for 20 hrs., cooled, weighed, burned in a Pt crucible for 8 hrs. and the ash dissolved in 0.5 N HCl. Twenty-five cc. of this soln. were used for the detn. of Mg by the Kramer method (cf. *C. A.* 15, 3858). The Mg content in 25 sound teeth ranged from 0.554 to 0.764, av. 0.649%, and in 25 decayed teeth the range was 0.825 to 1.585, av. 1.154%. Expts. with guinea pigs showed that extensive decalcification of teeth and of some parts of the bones is induced by scorbutic feeding while calcification occurred when the animals were fed sufficient antiscorbutic food. It is questioned whether in all cases recalcification is wholly due to the diet. It may be that tissue degeneration proceeds to the point of calcification. Among other abnormal conditions which occur as a result of protracted antiscorbutic deficiency is the effect on the eye. A slight scorbutic effect on pregnant mothers has resulted in the absence of one or both eyes in the young. Animals on a scorbutic diet invariably have eye trouble which is cleared up by feeding orange juice. With all the proper food factors supplied except the antiscorbutic, the animal organism appears to withdraw Ca from the teeth and from some parts of the bone. L. W. RIGGS

Effect of defective diets on teeth. Relation of calcium, phosphorus and organic factors to caries-like and attaching-tissue defects. C. J. GRIEVES. *J. Am. Med. Assoc.* 79, 1567-73(1922).—The results of feeding rats various diets failed to connect definitely any particular dietary deficiency with the occurrence of dental caries. Until further facts are available one can think only of the necessity for a proper Ca-P-org. factor balance in any diet as most important in the formation and maintenance of normal bones, teeth and attaching tissues. L. W. RIGGS

ABNORMAL

The action of artificial sunlight on metabolism. W. LASCH. *Deut. med. Wochschr.* 47, 1063(1921).—Children with rachitis were exposed to the rays of artificial sunlight. A marked increase in the retention of Ca and P resulted. S. AMBERG

Metabolism in tetanus. ERICH KRAUSS. *Klin. Wochschr.* 1, 1354-7(1922).—In tetanus the total N excretion in the urine is markedly increased. By far the largest percentage of the N increase is due to urea. Of the other nitrogenous components creatinine shows the largest increase while the concns. of NH_3 and uric acid are only slightly increased. MILTON HANKE

Use of vegetables in the diabetic diet. HILDA M. CROLL. *J. Am. Med. Assoc.* 79, 1424-6(1922).—Tables are given showing the carbohydrate content of thrice boiled vegetables, and showing 2 daily dietaries for patients with severe diabetes. By using a large amt. of water in the boiling the reducing substances may be more completely removed and the amt. of vegetables in the diet increased. It is important to improve

the flavor of thrice boiled vegetables by proper seasoning in order that the patient may be willing to keep within the necessary food limits.

L. W. RIGGS

F--PHYSIOLOGY

ANDREW HUNTER

A critical examination of current views on internal secretion. SWALE VINCENT. *Lancet* 192, II, 313-20.

E. B. FINK

Demonstration of the enzymic solution of coagulated proteins with the immersion refractometer. E. KUPFLWIESER. *Biochem. Z.* 131, 413-72(1922).—An extensive and painstaking study of the sources and degree of error in the particular instrument used. The conclusion is made that under the conditions of the expts. reported an increase in the refractive index of 0.00010 can be taken as a sign of enzyme activity in mixts. of serum and substrate. Results of detns. made under identical conditions agree within a limit of error of ± 0.00005 .

F. S. HAMMETT

Acid hemolysis and the effect of calcium. A. JARISCH. *Biochem. Z.* 131, 547-59 (1922).—Sheep blood corpuscles were washed free from serum with 0.9% NaCl, suspended in isotonic CaCl_2 soln. and treated with increasing amts. of HCl. It was found that a concn. of HCl slightly greater than that sufficient to produce hemolysis causes the corpuscles to settle out of suspension, to be colored brown, and that no hemolysis occurs. The corpuscles so produced do not go into soln. when treated with hemolytics and appear as if fixed. Inspection with the ultramicroscope shows that an internal coagulation has taken place. The cause of this coagulation is supposed to be an acid pptn. This coagulation is also seen, but to a lesser extent, in Ca-free suspensions; the presence of Ca then strengthens the process since it hinders the loss of hemoglobin. This indicates that the coloring matter participates in the pptn. In this effect Ca is only replaceable by Sr, Ba and Mg. The isoelec. point of the stroma proteins, as well as of the intact corpuscles, was found to be variously placed when various regulators are used, thus explaining the contradictory findings in the literature. The optimum pptg. point of the stroma in dissolved blood as well as the cataphoretic point of the intact corpuscles in acetate and lactate mixts. was found to be at a p_H of about 5.0; in phosphate mixts. at about a $p_H = 3.2$.

F. S. HAMMETT

The distribution of chlorine between blood corpuscles and plasma and the influence of the carbon dioxide tension. Z. DISCHE. *Biochem. Z.* 131, 596-600(1922).—Blood was drawn from the veins of fasting subjects and was either defibrinated or treated with 1 to 2 g. Na citrate for each 100 cc. Neither the corpuscles of circulating blood nor blood from which the CO_2 has been driven contain Cl in normal persons. On the other hand, in certain cases of renal disease and hypertonia it was found that the corpuscles contained Cl in significant amts. The Cl content of the serum of these cases is of the same order of magnitude. Hence the presence of Cl in the corpuscles is a sign of pathol. swelling process.

F. S. HAMMETT

The replaceability of potassium by uranium in striated muscle. (The quieting of the fibrillary contractions in sodium chloride solution.) F. VERZÁR AND W. SZÁNYI. *Biochem. Z.* 132, 53-63(1922).—Observations were made of the effect of U and K salts on the fibrillations of frog sartorius muscles induced by immersion in 0.65% NaCl soln. It was found that $\text{UO}_2(\text{NO}_3)_2$, as well as KCl and KNO_3 , caused a stopping of the fibrillations from which it is concluded that U is a K substitute. The effect is reversible if the action has not been too prolonged, and is not due to a toxic decrease in irritability by U since a muscle irreversibly quieted is not particularly less sensitive to elec. stimulation. The antagonistic action of K and U salts towards NaCl is not based on equiv. radioactivity but on equimol. concn. of the solns. Hence this effect of the U salts seems to be mol. or ionic rather than radioactive as is the action on the heart. An increase

in the concn. of the NaCl soln. can be compensated by increase in the concn. of the K- or U-salt soln. Attempts to influence the fibrillations by radiation were unsuccessful. The same paradoxical effect as observed by Zwaardemaker on the heart was obtained, *e. g.*, a stimulation when K- and U-salts were present at the same time. Finally it was shown that not only U salts but also other protein precipitants, such as HgCl and HCOH, are able to quiet muscle fibrillating in NaCl soln. and that the reaction is reversible. It would appear from this as if the action of U is derived from its protein pptg. properties, or its effect on the plasma membrane. The reversibility is explicable on this basis. The K salts must produce their effects through the mols. and ion action as well as by their radioactive properties, and their action is of a nature to induce a thickening of the plasma membrane.

F. S. HAMMETT

Tension and extensibility on acid contracture and chemical contracture of muscle. F. VERZAR, J. BÖGEL AND W. SZÁNYI. *Biochem. Z.* 132, 64-81 (1922).—The contracture of muscle under various chem. treatments was studied. It was found that contraction induced by acids is quite opposite to natural contraction in that it is accompanied by only a very low tension. On the other hand, in contracture induced by protein pptn. a significant degree of tension occurs. The extensibility of muscle is increased over the norm. during acid contracture. The apparent work performed in acid contracture is less than the max. natural performance. That which takes place on protein pptn. contracture or H₂O deprivation is greater. Rigor mortis has a certain similarity to acid contracture.

F. S. HAMMETT

The potassium-calcium equilibrium in the animal system. H. ZWAARDEMAKER. *Biochem. Z.* 132, 95-102 (1922).—A consideration of the various points of view current in the literature leads Z. to the opinion that if the theory of ionic equil. is to be considered from the point of view of colloid chemistry a 3-fold equilibration is indicated, *e. g.*, the light metals: Ca, Ca: heavy metals and light metals: heavy metals. The radioactive heavy metals have no place in the comparison, heavy metals: light metals, since they are true antagonists, while in equilibration the condition is recognizedly one of pseudo-antagonism. The phenomena of radio-physiology can, in the meantime, not be explained on a purely colloid chem. basis.

F. S. HAMMETT

The action of artificial light on alveolar carbon dioxide tension. S. ÉDERER. *Biochem. Z.* 132, 103-9 (1922).—Radiation of man by means of a quartz lamp produces different effects on the CO₂ tension of alveolar air according to the strength of the dosage administered. Weak stimulation has no effect; radiation of medium intensity increases the CO₂ tension and strong leads to a lowering. The action of this type of artificial illumination on the CO₂ tension is independent of the erythema of the skin. The hypercapnic effect is not of central origin, for the organism as a whole becomes oversensitive, but is probably hematogenous. This interpretation is based on a probable increase in the alk. of the blood, a decrease in the acid products of metabolism and a change in the colloid state of the blood proteins.

F. S. HAMMETT

The mass law relationships between the true reaction of the urine and the alveolar carbon dioxide tension. G. ENDRES. *Biochem. Z.* 132, 220-41 (1922).—The variation in the p_H of the urine during the course of the day was followed and compared with the CO₂ tension of arterial blood (alveolar air). Both the p_H of the urine and the CO₂ tension vary, after eating, in that direction tending to regulate the reaction of the blood. The jog in the curve for the one occurs synchronously with the jog in the curve for the other and the magnitude and time of occurrence are influenced by the duration of the meal. The characteristic of the post-digestive rise in both curves is related to the type of food among other things. On a meat diet the rise and fall are more steep and rapid than when a carbohydrate diet is taken. Hasselbach's interpretations of the post-digestive decrease in urinary acidity were refuted. It appears quite

probable that the HCl secretion of the stomach is of great significance for the drop in the curve since in cases of an acidity the post-digestive alterations do not take place. The daily level of the curve depends on the type of food. In sleep the curves for the 2 factors measured run an almost parallel course and the increase in urinary acidity appears to be related to the decreased sensitivity of the respiratory center. When morphine is administered the curves tend to diverge from each other, while on the other hand they tend to converge when caffeine is given. Spontaneous alkaliuria is related somewhat to the type of food ingested but nevertheless an altered irritability of the respiratory center comes into play in many cases. The response of both the CO_2 tension and urinary p_{H} to muscle activity is the same and consists in a marked steep rise, followed by a steep fall slightly below norm. and a relatively slow recovery. The increase in p_{H} and CO_2 tension after bleeding reaches its max. after about 2 hrs. and the return to norm. value takes place in the second 2-br. period. This may be due to the decrease in erythrocytes.

F. S. HAMMETT

The biological action of lymph-gland extracts on smooth muscle tissue, the heart and the blood pressure. O. WIRTH. *Biochem. Z.* 132, 245-69(1922).—Water and alc. exts. of lymph glands from different animals and different portions of the body were tested *in vivo* and *in vitro*. All H_2O exts. whether obtained by cold or hot extn. or from fresh or heated tissue had the same qual. effect on surviving tissues containing smooth muscle. The isolated blood vessels reacted as towards adrenaline by contraction, save the coronary artery of the ox which relaxes. The vessels of the hind legs of the frog were dilated by both weak and concd. solns. The intestine, and virgin and gravid uterus responded with an increase in tone. The alc. exts. differed both quant. and qual. from the H_2O exts. The isolated blood vessel strips contracted. The vessels of the hind leg of the frog dilated after weak doses; dilated and then contracted or *vice versa* after medium dosage and contracted when concd. doses were given. This latter contraction was followed by a dilatation. The tonus of the intestine and uterus was raised. An analysis of the qual. reaction of the 2 exts. on the coronary artery demonstrated the presence of 2 antagonistic principles. The extn. of the H_2O ext. with Et_2O causes a sepn. of the hypotonic element from the hypertonic, as present in the alc. ext. The effect of the H_2O and alc. ext. on the curarized frog heart *in situ* was studied in detail. Two phases occur. In the 1st there is a decrease in amplitude of contraction and slight decrease in tonus. In the 2nd phase the frequency decreases while the amplitude increases. Hearts that are beating badly can be stimulated to stronger function by the application of lymph-gland ext. There is no general antagonism between adrenaline and lymph-gland ext. The action of the alc. ext. simulates that of choline. The blood pressure is lowered on exhibition of the exts.

F. S. HAMMETT

Studies of blood cells. I. Acid treatment of blood cells. L. KARZAG AND F. STERNBERG. *Biochem. Z.* 132, 279-83(1922).—Studies were made of the decolorization of the various white cell types by the action for 5 min. of HCl of various concns. The cells were stained with Jenner-Giemsa soln., Fuchsin S., brilliant green, and crystal violet. They were first fixed in H_2O -free MeOH for 1 or 2 min. and the acid allowed to act for 5 min. It was found that the stained nuclei possess a varied resistance to HCl. In general the histogenetically younger cells were more easily decolorized. The least resistant were the myeloblasts and the myelocytes; the more resistant were the leucocytes and lymphocytes and the most the normoblasts. The sensitiveness to acid appeared to be in inverse relation to the acid concn. The resistance of the erythrocytes is enhanced by staining. II. The behavior of blood cells towards hydrogen peroxide. *Ibid* 284-7.—Pure, neutral dil. H_2O_2 produces a disintegration of fixed but unstained preps. of myeloblasts, myelocytes, polynuclear cells and lymphocytes, while normoblast nuclei and erythrocytes show great resistance toward this reagent. The staining

capacity remains in spite of the loss of structure. The harmful action of H_2O_2 appears to be due to a deep-seated chem. change in the protoplasm and nuclear protein by atomic O. This is probably brought about by the oxidases of the cells. Age and maturity of the cells play an important role since brief treatment with H_2O_2 gives the following series of increasing resistance: myelocytes, myelohlasts, Gumprecht's nuclei, polynuclear cells, lymphocytes. Hemoglobin within the cell is unattached; when, liberated by hemolysis it is decolorized easily. The treatment of the cells after polychromatic staining leads after a time to a noteworthy change in the color nuance and cell form, thus indicating changes in oxidase activity. The results seem to show that the oxidase content, sensitivity to O and acid vulnerability are related properties of blood cells. III. The use of methods of catalytic oxidation in microscopic work. L. KARCZAG, F. STERNBERG AND J. HALMT. *Ibid* 288-92.—The catalytic oxidation of fixed unstained blood preps. with H_2O_2 and Mn oxidizers showed that the protoplasm and nuclear protein are unaffected by such treatment. The catalytic oxidation of dyes showed that active O₂ attacks the dye and not the protein. The acidophile elements are particularly resistant to active O₂ while the basophile elements are sensitive. This behavior of the blood cells, *e. g.*, the cell constituents, appears to be conditioned by the manner of union between cell and dye. The union between dye and acidophile basic substance is exceptionally firm and hence is resistant to active O₂. The catalytic oxidation of dyes can therefore be followed not only *in vitro* but also in stained microscopic preps. (*Bacillus tuberculosis*, acidophile elements) and can be used as a new method of differentiation. F. S. HAMMETT

A new substance extracted from the thyroid. U. SAMMARTINO. *Biochem. Z.* 132, 293-4(1922); cf. C. A. 16, 3948.—Four hundred g. of fresh horse thyroid glands freed from fat were minced and cooked twice with H_2O acidified with AcOH. After each beating the liquid was squeezed from the tissue. The liquor gave no ppt. with AcOH nor basic Pb acetate. The liquor was concd. in vacuum and could then be pptd. with Pb acetate. The Pb ppt. was removed, the soln. dild. to prevent colloidal pptn. of PbS, and the excess Pb removed by H_2S and the latter by CO_2 . The filtrate when concd. in vacuum to 20 cc. gave a gelatinous substance yielding no tryptophan reaction. The gelatinous mass was dissolved in boiling H_2O , filtered, and alc. was added as long as a ppt. formed. The filtrate from this ppt. was pptd. with alc. picric acid and the crystals were recrystd. from boiling H_2O . No m. p. could be obtained. Ashing with H_2SO_4 in Pb gave evidence that the compd. was K picrate. A few small red crystals were obtained from the concn. of the mother liquor. These also gave no m. p. Further crystn. gave picrate crystals m. from 255 to 295° on the Maquenne block. The picric acid was removed from the mother liquor by extn. with Et_2O , abs. alc. was added and a cryst. substance obtained. This was dissolved in boiling H_2O , repptd. with abs. alc. and dried in vacuum; it now m. 225-228°. The substance contained no halogen, S or P. It was the Ca salt of an N-contg. O-rich compd. with the empirical formula of $C_{14}H_{12}N_2Ca_2O_{14}$, as calcd. from the following analysis: C, 28.52%; H, 5.26%; N, 4.69% and Ca, 21.81%. F. S. HAMMETT

Is glucose a normal constituent of the erythrocytes as they circulate in the blood of man? MARTIN BRANN. *Klin. Wochschr.* 1, 1103-4(1922).—The concn. of glucose in the erythrocytes is approx. identical with that in the plasma, namely 0.06 to 0.13%. In some cases the concn. of glucose is identical in whole blood, plasma and erythrocytes. In the majority of cases the concn. of glucose in the erythrocytes is somewhat lower than that in either whole blood or plasma. MILTON HANKE

The glucose permeability of the liver. F. GEIGER AND O. LOEWL. *Klin. Wochschr.* 1, 1210(1922).—When the livers of winter frogs are perfused with a nutrient soln. contg. glucose some of the glucose is removed by the liver cells. Glucose is not consumed

by the liver cells when the perfusion liquid contains soap in concns. as low as 1 : 100,000. When such frog livers are perfused with normal blood serum, from 5 to 11 mg. of glucose are consumed in 0.5 hr. Not a trace of glucose disappeared from diabetic sera under identical conditions. Diabetic sera may contain substances that, like soap, prevent the assimilation of glucose by the liver cells. MILTON HANKE

The role of the bile in uric acid metabolism. Preliminary report. THEODOR BRUGSCH AND JULIUS ROTHER. *Klin. Wochschr.* 1, 1495-6(1922).—Uric acid is excreted not only in the urine but also in the bile. The exact amt. excreted in the bile and the relation of this to the urinary excretion are not given. MILTON HANKE

Leucocytic secretions. ALEXIS CARREL AND A. H. EBELING. *J. Exptl. Med.* 36, 645-59(1922).—The serum obtained from cultures of leucocytes is less inhibiting for homologous fibroblasts than the serum from media without leucocytes. In some expts., its hemolytic action on sheep or rabbit erythrocytes is also increased. The addition of casein to leucocytic cultures brings about a decrease in the inhibiting effect of the serum on homologous fibroblasts. The increase in the activity of homologous fibroblasts in serum obtained from leucocytic cultures is probably due to growth-promoting substances secreted by the leucocytes. The presence of a foreign protein under certain conditions detrs. a more abundant leucocytic secretion. C. J. WEST

G—PATHOLOGY

H. GIDEON WELLS

Mesencephalitis epidemica (encephalitis lethargica). F. UMBER. *Deut. med. Wochschr.* 47, 261-3(1921).—The cerebrospinal fluid of 36 cases of encephalitis lethargica was examd. for urea, indican, creatinine, and undetd. N. In 5 cases the values of high norm or above were found. Since there were no kidney lesions increased intermediary protein decompn. is assumed with formation of toxic products. S. A.

Remarks about the precipitation reactions of Sachs-Georgi and Meinicke (III modification) and the turbidity reaction of Dold. R. STREMPER. *Münch. med. Wochschr.* 69, 85-6(1922).—The Dold reaction was sometimes negative when the others were positive and there was clinical lies. S. AMBERG

Is the glycerol reaction of Gabbe an indicator of the lipid content of the blood after injections of body foreign substances? B. ENGELMANN. *Münch. med. Wochschr.* 69, 120(1922).—In the test 0.5 cc. fresh serum is stratified with 5% glycerol soln. and incubated 24 hrs. at 37°. A ring formation (turbidity) means a positive test. It is shown that on feeding 30-50 g. fat the serum becomes turbid and gives a good reaction. Injection of body foreign substances on fat-free food hardly ever causes a positive reaction. S. AMBERG

Experimental investigations on the mode of action of proteins and stimulating substances. I. Fixation of poison and hypersensibility. DÖLKEN AND R. HERZGER. *Münch. med. Wochschr.* 69, 185-9(1922).—Proteins, such as milk and sera, etc., were mixed with drugs such as strychnine, nicotine, morphine, etc., and then injected into rabbits, or proteins were injected first and later on the poisons. The effect may be to increase or decrease the toxicity. The expts. are to be published *in extenso* elsewhere. (This paper contains many interesting data.) S. AMBERG

The contents of vesicles above specific reactions. II. Filling of skin vesicles. F. THOMAS AND W. ARNOLD. *Münch. med. Wochschr.* 69, 196-7(1922).—Skin vesicles were obtained thus: In individuals giving a positive intracutaneous tuberculin reaction cantharidine was applied over the reaction spot 36 hrs. after its production. The vesicle contained substances which increased the local tuberculin reactions in tuberculin-sensitive individuals. This substance is destroyed in the water bath at 60° during 1/2

hr. Vesicles produced over a non-specific local inflammation had inactive contents.

S. AMBERG

Cholemic lipemia. BUERGER. *Münch. med. Wochschr.* 69, 103-6(1922).—Cholesterol detns. were made by the Windaus method. Bilirubin was detd. according to Hijmans van den Bergh. The total fat was obtained by pptg. the serum with 10 times its vol. alc., washing the coagulation well with alc. and ether, and dissolving the residue of this soln. in petr. ether. Free and combined cholesterol were detd. In cases of mechanical icterus a latent cholemic lipemia was found, that is, an increase of the total fat of serum including lipoids without a turbidity of the serum. From the norm. of about 0.4-0.5% fat, values up to 2.2% were obtained. In cases of hemolytic icterus total fat and cholesterol are not increased. In cases of cholemic lipemia an increase in cholesterol precedes the increase in glycerides. With increasing duration of the bile occlusion the esterification of the blood cholesterol becomes less, so that less than $\frac{1}{3}$ of the cholesterol may be in combined form, instead of $\frac{2}{3}$ or more. In certain cases of icterus an increase of bilirubin may occur without increase in cholesterol. S. A.

The permeability of the capillaries in man. M. GÄNSSLEN. *Münch. med. Wochschr.* 69, 263-4(1922).—Vesicles were produced in men by means of cantharidine, under various conditions and glucose was detd. in the vesicle content. Without and with administration of glucose the vesicle glucose content was found higher than the glucose content of the blood. The residual N in normal individuals was on the av. 40 mg. with similar values for the blood. The vesicle content was also examd. refractometrically.

S. AMBERG

Cholesteroluria and indigouria. G. DORNER. *Münch. med. Wochschr.* 69, 661 (1921).—In a case of double cystic kidney cholesterol crystals were found in the urine and in a 2nd case of kidney stones, there were cholesterol crystals and blue masses in small needles, scales, and in the amorphous form. These were found in freshly voided urine. The removed kidney stones contained also cholesterol, chiefly Ca oxalate and carbonate, besides indigo. The blue masses were sol. in CHCl_3 .

S. AMBERG

The use of Arion extracts in the so-called Hecht modification of the Wassermann reaction. W. LOELE. *Münch. med. Wochschr.* 69, 885-8(1922).—In the Hecht modification of the Wassermann reaction (use of the hemolysin which occurs in the blood of the patient) an ext. of snails (*Arion rufus*) which has been kept in 10% formol can be used. For detail see the paper.

S. AMBERG

The value of concentration determinations of the cerebrospinal fluid in diseases of the central nervous system. G. WÜLLENWEBER. *Münch. med. Wochschr.* 69, 927-9(1922).—Detns. with the interferometer on cerebrospinal fluids. S. AMBERG

The inhibiting action of saponin on the lues precipitation reactions (Sachs-Georgi-Meinicke reaction) as well as on the precipitation reaction of Sachs-Guth for the demonstration of heterogeneous antibodies in contradistinction to the negative effect of saponin on the precipitation reaction of Uhlenhuth. P. NIEDERHOFF. *Münch. med. Wochschr.* 69, 929-30(1922).—Saponin is supposed to act on the ext. lipoids, preventing their dehydration. It does not act on Uhlenhuth pptn. because the ppt. here is probably composed of proteins. HCHO prevents all the reactions, probably by acting on the pto-teius necessary for the reactions.

S. AMBERG

Investigations on protective enzymes. G. BLUNCK. *Münch. med. Wochschr.* 69, 1005-7(1922).—It was possible to dye organs to be used for the Abderhalden reaction with Metachromviolet R, so that they yield color to added serum only when a digestion takes place. This method is much more convenient than the Abderhalden dialysis method. The organ freed from blood is put in 25 times its amt. of distd. H_2O . About 3% (of the wt. of the organ) of the dye is dissolved by boiling in a little water with

addn. of 1% NH_4OH and the soln. added to the organ. Metachrome "beize" (double amt. of dye) dissolved hot is also added. The whole mixt. is slowly heated so that it boils in about 1 hr.; it is then kept boiling gently 2 hrs. with replacement of the evapd. water. The excess dye soln. is poured off through a sterile sieve and is washed several times with sterile water. The dyed substratum is kept in sterile water under toluene or dried at 40° *in vacuo* and sterilized dry. The serum when positive becomes reddish blue; it may be made alk. by addn. of a drop of 1% $(\text{NH}_4)_2\text{CO}_3$. It is necessary to prep. the organs very carefully and to work under sterile conditions. The reactions were sp. Autolytic enzymes and protective enzymes act in the same way. This was shown with enzyme pptd. from placenta. Placenta freed from blood was minced, toluene, and 2 parts Ringer soln. being added and extd. 8 hrs. with water of 45° in a vacuum extn. app. $(\text{NH}_4)_2\text{SO}_4$ in satd. soln. is added to 30% $(\text{NH}_4)_2\text{SO}_4$. The ppt. is filtered off and the soln. brought to 70% $(\text{NH}_4)_2\text{SO}_4$. Another ppt. forms which contains the enzymes. The ppt. is dissolved in water and again pptd. with about 10 vol. alc. and filtered off with suction after several hrs. The residue is taken up with a little 50% glycerol, extd. 24 hrs. and filtered. The residue of this is again extd. with glycerol. The united exts. are pptd. with 5 vol. alc. and washed free from glycerol with 70% alcohol. The ppt. is dried in the vacuum desiccator. S. AMBERG

Blood pressure studies in diabetes mellitus. JACOB ROSENBLUM. *Proc. Soc. Exptl. Biol. Med.* 18, 236-7(1921).—Records for periods up to 10 yrs. (in some cases) disclosed normal or slightly subnormal pressure in uncomplicated cases. In acidosis the pressure falls. Glucemia has no effect on blood pressure. C. V. B.

Observations on the excretion of sugar in the urine in health and disease. LUDWIG KAST AND H. M. CROLL. *Proc. Soc. Exptl. Biol. Med.* 19, 84(1921).—The av. daily excretion of reducing sugar was detd. to be 0.59-1.14 g. in 4 normal adults. In 116 cases diagnosed as neurasthenia, hyper- and hypo-thyroidism, nephritis, hypertension, arthritis, and various cardiac disturbances, the daily excretion seemed to be normal, the patients being on ordinary diet. When diabetics are "sugar free," the daily excretion is practically normal. The acetone-picric acid method of Benedict and Osterberg was used. C. V. B.

Antiketogenesis. A. I. RINGER. *Proc. Soc. Exptl. Biol. Med.* 19, 97-9(1921).—Diabetic animals were fed chem. compds. that may play a role in the intermediary metabolism of carbohydrates. These substances may be divided into 2 classes. The 1st or glycogenetic class consists of substances like glyceraldehyde, dihydroxyacetone pyruvaldehyde, pyruvic and lactic acids, which, when fed to diabetic animals, are completely and directly converted to glucose and excreted in the urine. In the body, the reaction from the one to the other is reversible, but tends towards glycogenesis in the diabetic. The 2nd class consists of substances like AcH and perhaps EtOH . They possess marked antiketogenetic powers. Their reaction from the 1st class is irreversible. In diabetes these metabolites pass with difficulty from the 1st to the aldehyde class in which they are capable of exercising antiketogenetic powers. C. V. B.

Determination of optimum amount of antigen in complement-fixation tests. R. L. KAHN AND S. R. JOHNSON. *Proc. Soc. Exptl. Biol. Med.* 19, 128(1921).—The antigen unit giving complete fixation with positive sera is detd. The usual quantity of weakly positive serum is pipetted into a series of 10 tubes, to the first of which is added $1/4$ antigen unit, the quantity is doubled in succeeding tubes, the last tube receiving 10 units. After fixation and addition of sensitized cells, the tube displaying the maximum fixation shows the optimum amount of antigen to be used in the daily tests. C. V. B.

Functional tests of the external secretion of the pancreas from studies of the duodenal juice. E. DELNICH. *Arch. Verdauungs. Krankh.* 20, 27-41(1922).—Previous

differences in quant. enzyme detn. are due to dissimilarity in method. D. introduces 30 cc. 0.1 N HCl into the duodenum and finds that the normal person secretes 35-65 cc. in from 40 to 60 min. with an acidity of 3-5 for 100 cc. duodenal contents. In 18 cases of ulcers of the ventriculus and the duodenum, 7 showed hypersecretion, and 2 hypochylia. Hypachylia or achylia of the pancreas was never found in depressed gastric secretion.

F. S. HAMMETT

Amboceptors and receptors. II. J. MORGENROTH AND R. BIRLING. *Biochem. Z.* 131, 525-40(1922).—Tissues from the mouse are tested against rabbit, guinea pig and goat serum and the sera against each other. Goat blood possesses a receptor group which is not present in the organ cells of mice or guinea pigs; it is called Receptor A. Goat blood also contains a receptor group which is present in the organ cells of these other species and is called Receptor B. Mouse erythrocytes do not contain the B-receptor but only the C-receptor which is not present in goat blood and tissues of guinea pigs, mice, etc. On the other hand, goat blood contains a receptor group D, which is not present in the organ cells of the various animal species and mouse blood but is present in the red cells of sheep. Hemolytic immune sera, which have been obtained from different animal species by means of the same antigen, show a varied acidity. Hemolytic sera under like conditions are just so much the more avid, the smaller the receptor difference between antigen and serum donor. The avidity of a hemolytic serum is dependent on the antigenic properties of the organ cells of the serum donor.

III. **Intravital fixation of cell antihodies.** *Ibid* 541-6.—The injection of inactive rabbit serum, which has been previously treated with mouse corpuscles, into the mouse produces an intravital hemolysis with hemoglobinuria and hemolytic icterus. This phenomenon occurs, although the complement end-piece is lacking in the mouse serum. Lethal doses of mouse-tumor-rabbit serum in general do not have fatal effects in carcinomatous mice; if death is produced it is delayed. The injected cancer antihodies are taken care of by the cancer cells of the body.

F. S. HAMMETT

Ammonia excretion in hunger osteopathy and chronic undernutrition. D. ADLERSBERG. *Biochem. Z.* 132, 1-17(1922).—Hunger osteopathy is the last link in the chain of war and post-war diseases. The first cases were observed in Vienna early in 1919 while the disorder was reported from Russian-Poland in 1917. Analyses of 24-hr. specimens of urine from patients with this disease showed the following av. characteristics: vol. 2190 cc., d. 1.015, total N 7.609 g., NH_3 0.776 g. Although a N balance was not obtained A. is of the opinion that there exists a relatively increased NH_3 excretion. The administration of relatively great amts. of NaHCO_3 induces a significantly greater decrease in NH_3 excretion than was to be expected on the basis of previous expts. These findings can be utilized as a means of differential diagnosis from osteomalacia. Similar observations were made in cases of chronic undernutrition. An increase in the acidity of the blood could not be detected. The increased NH_3 excretion in these disorders is considered as a protective action of the organism.

F. S. HAMMETT

The chemical nature of toxins and antitoxins. E. SALKOWSKI. *Biochem. Z.* 132, 84-8(1922).—S. was able to conc. diphtheria antitoxin from serum by satn. with finely pulverized NaCl, adding double the vol. of satd. NaCl soln. and pptg. with CCl_3COOH either as such or in 10% NaCl. About 1 g. of CCl_3COOH is required for each 30 cc. lot of liquid. After standing a half hr. the mixt. is filtered and the ppt. washed with satd. NaCl with shaking and freed as much as possible from adhering liquid. It is then mixed with H_2O by grinding and filtered after half an hour. The clear filtrate is a practically protein-free soln. of the antitoxin which can be concd. in vacuum after neutralization of the residual CCl_3COOH with Na_2CO_3 . Only 20% of the active antitoxin is, however, obtained by this process. The product never induces an exanthema

such as the serum sometimes does. The freedom of the prepn. from protein would make its use in parenteral injection safer than serum. F. S. HAMMETT

Activators of fermentation. E. LINDBERG. *Biochem. Z.* **132**, 110-34(1922).—These fermentation studies were carried out with weighed amts. of fresh, dried and washed yeast. Two strains were used. All the fermentation mixts. were brought to a p_H of about 5.0 by a phosphate mixt. The CO_2 evolution was used as a measure of the reaction rate. It was found that the following prepn. and substances accelerated fermentation: wash water from fresh and washed yeast; coenzyme from fresh and phosphate-washed dry yeast; milk. Abietic acid, amyriac and cholesterol had no activating effect. The activating effect of the milk catalyst of fermentation is increased by mixts. of nutrient salts, unless in excess. When the fats of milk are extd. the catalytic properties remain and hence are not confined to the fats. A p_H of about 5.0 was found to be the optimum for self fermentation of the yeasts employed. Further studies with pyroreacemic acid and Na pyruvate are reported. F. S. HAMMETT

The pentose of a new case of pentosuria. A. N. WRZESNEWSKI. *Biochem. Z.* **132**, 135-7(1922).—The $[\alpha]$ of the urine of a patient showed the presence to 0.2 to 0.3% carbohydrate as glucose while the reduction test gave from 0.72 to 0.87%. The $[\alpha]$ disappeared after fermentation of the urine with yeast but there was still 0.48% sugar present. The orcinol and phloroglucinol tests were strongly positive both before and after fermentation. W. was able to isolate from 24 l. of the urine a white cryst. substance m. 202-204°, which contained 8.5% N and appeared identical with racemic arabinose diphenylhydrazone of a calcd. N% of 8.9. The osazone was also pptd. direct. It melted at 162-164° and contained 17.3% N as against a theoretical 17.1%. Since both prepn. gave no $[\alpha]$ and since Zerner and Walktuch's test (*C. A.* **8**, 749) was negative U. concludes that he was dealing with inactive arabinose. F. S. HAMMETT

The present status of serum therapy. ULRICH FRIEDEMANN. *Klin. Wochschr.* **1**, 1056-60(1922). MILTON HANKE

The separation of the Wassermann aggregate and the possibility of making use of this separation in substantiating a positive Wassermann reaction: A. v. WASSERMANN AND H. CITRON. *Klin. Wochschr.* **1**, 1101-3(1922).—When an antigen treated luetic serum is filtered through a specially prepared kieselguhr filter, the antigen is separated from the antibody. The antibody appears in the filtrate; the antigen adheres to the filter. Other absorbing substances such as charcoal, ZnO , kaolin, and $BaSO_4$ do not effect such a sepn. MILTON HANKE

The origin of gallstones. L. ASCHOFF. *Klin. Wochschr.* **1**, 1345-9(1922).—A review. MILTON HANKE

The appearance of the aldehyde reaction in the urine after the per oral ingestion of chlorophyll. W. FALTA AND F. HÖGLER. *Klin. Wochschr.* **1**, 1357(1922).—The ingestion of 45 cc. of a 10-15% alc. soln. of chlorophyll by hepatopathics is followed by the excretion, in the urine, of substances that give the positive aldehyde reaction. A positive reaction is also obtained in such cases after the ingestion of 3 g. of dried bile. MILTON HANKE

The diagnostic value and the etiology of the experimental glucosuria of pregnancy. H. A. DIETRICH. *Klin. Wochschr.* **1**, 1403-7(1922).—A review. MILTON HANKE

Acute yellow atrophy of the liver. GOTTHOLD HERXHEIMER. *Klin. Wochschr.* **1**, 1441-6(1922).—A review. MILTON HANKE

Variations in the heat coagulation temperature of blood serum. R. L. MAYER. *Klin. Wochschr.* **1**, 1693(1922).—0.2 cc. of the serum was introduced into a U tube having an internal diam. of 3 mm. The tube was attached around the bulb of a thermometer and held in place with rubber bands. The tube plus thermometer was then

placed in a gas-heated water bath whose temp. was 70° at the time of immersion. The heat was regulated so that a rise in temp. of 10° was obtained in 2.5 min. Normal sera were found to coagulate solid at a temp. of 73.5–75.5°. None of the sera investigated coagulated below 73°; but an occasional pathol. serum was found to coagulate at 91° and in one case no coagulation had occurred at 98°. In the latter cases chemical detns. showed that the sera had an abnormal protein content. Most sera became cloudy a few degrees below the coagulation temperature, but a few samples coagulated without becoming cloudy.

MILTON HANKE

The value of the heat coagulation temperature of serum as a clinical procedure. GEORG ROSENOW. *Klin. Wochschr.* 1, 1694(1922).—The serum of patients afflicted with diseases that are associated with a retention of water or an abnormal excretion of salts that leads to concn. changes in the blood serum coagulates at abnormally high temps. (see preceding abstr.). Examples of this class are diabetes (78.5°), multiple myeloma (76.5°), carcinoma (76°), decompens vitium (77.5°), secondary anemia (76.4°), arhythmia perpetua (76.5°), chronic icterus (82°), and chronic nephritis (83–92°). The normal coagulation temp. is 73–75°.

MILTON HANKE

Opsonins and diets deficient in vitamins. G. M. FINDLAY AND RONALD MAC-KENZIE. *Biochem. J.* 16, 574–77(1922).—Rats fed on diets deficient in vitamins A and B, and guinea pigs fed on a diet deficient in vitamin C, do not show any decrease in the opsonic activity of the serum. The phagocytic activity of the polymorphonuclear leucocytes of guinea pigs with chronic scurvy is not decreased.

B. H.

Bacterial agglutination in diseased blood. JOSEF VORSCHÜTZ. *Centr. Bakt. Parasitenk., I Abt.* 88, 394–401(1922).—In 52 patients suffering with various infective diseases the blood serum became altered so that it agglutinated typhoid, paratyphoid B, dysentery and the Widal "Fleisch vergifter" bacilli and agglutinated red cells. The Breslau and Gärtner bacilli bear a different elec. charge and are not agglutinated. All bacteria are agglutinated by quinine-HCl. The agglutination of bacteria by patient's serum is independent of the concn. of globulin. Hemagglutinins are identical with bacterial agglutinins. When the globulins are pptd. as a result of preserving in ice, the agglutinins disappear. Typhoid serum produces hemagglutination as well as a Widal reaction. In many infective diseases the Widal reaction is of no use for the diagnosis of typhoid or dysentery. The diagnosis must be made from clinical symptoms or cultures.

JULIAN H. LEWIS

The practical use of blood indican estimation by the Joosse-Hass method. FRITZ EIGENBERGER. *Zentr. inn. Med.* 43, 445–7(1922).—With healthy kidneys, even with an extreme indicanuria, the blood indican is seldom increased. Acute diffuse nephritis always shows a normal value. In chronic nephritis 75% of cases show a high indicanemia especially if there is increased indican formation (constipation). The highest indicanemia occurs in uremia from chronic nephritis. In chronic nephritis with an increased indicanemia the rest N was 50–80 mg. per 100 cc. blood. The terminal stage of chronic nephritis shows the blood rest N was 70–230 mg. per 100 cc. blood. In hypertension with markedly increased blood indican the rest N was 60–150 mg. and with a slight indicanemia or none at all, it was 25–70 mg. per 100 cc. The blood indican goes parallel with the rest N except in acute cases and in cases where there is increased formation of indican. Hypertension without signs of renal inflammation, but which on autopsy revealed an arteriosclerosis of the kidney, showed in most cases only a high indicanemia when there was a high indican formation. It was higher the more marked was the heart insufficiency. In all cases of acute or chronic hemorrhagic nephritis without complication the blood indican was normal and independent of indican formation.

JULIAN H. LEWIS

Nitrogen retention in chronic interstitial nephritis and its significance. HILDING

BERGLAND. *J. Am. Med. Assoc.* 79, 1375-80(1922).—The following detns. were made: (1) The normal, min., max., and av. blood content of non-protein nitrogenous products from 12 young men. (2) The partition of creatine and creatinine between plasma and corpuscles in normal men. (3) The increase of the blood creatinine and the creatinine output in the urine after taking creatinine by mouth. (4) Increase (late) of the plasma-creatinine and corresponding creatine output caused by taking 4 g. creatine, the plasma-creatinine remaining constant. (3 subjects.) (5) Substantial uniformity in the retention of several nitrogenous waste products by whole blood, plasma and corpuscles. (7 cases.) (6) Comparison between waste nitrogenous products in the plasma and in the cerebrospinal fluid in nephritics and non-nephritics. The results which are shown in 8 tables are discussed at length. L. W. RIGGS

Value of the estimation of urea, non-protein nitrogen and creatinine as an index of renal function. W. A. FRONTZ AND J. T. GERAGHTY. *J. Am. Med. Assoc.* 79, 1383-4(1922).—Practically all of the information of clinical value gained by estns. of total N, non-protein N, uric acid and creatinine is furnished by the estn. of the blood urea content. Estn. of blood urea by the urease method of Marshall is accurate and comparatively simple. The excretory capacity of the kidney for the estn. of the total and separated function is best detd. by the phenolsulfonephthalein test. In certain cases of bilateral renal disease, the greatest amt. of information is obtained by an estn. of the blood urea and a measure of the excretory capacity by means of phenolsulfonephthalein. L. W. RIGGS

Significance of chemical blood findings in urologic conditions. J. B. SQUIER, C. G. BANDLER AND V. C. MYERS. *J. Am. Med. Assoc.* 79, 1384-6(1922).—The findings in 40 cases are shown in 6 tables. Preoperative information on the chemistry of the blood should be secured in all surgical conditions of the kidneys, bladder or prostate. The information is of more value in prostatic than in other urologic lesions. Of the different chemical blood tests, the urea is the most helpful, although with urea retention, the creatinine or CO_2 -combining power may be more significant. Patients presenting urea-N figures over 25 mg. per 100 cc. of blood should be operated on with caution, and best after a period of preliminary treatment directed to relieve the N retention. This applies especially to any lesion inhibiting the output of urine. L. W. R.

Concentration of urea in saliva. P. S. HENCH AND MARTHA ALDRICH. *J. Am. Med. Assoc.* 79, 1409-12(1922).—The ammonia and urea N were detd. by the urease method. The results of more than 130 analyses of saliva of normal and of nephritic persons are shown in tables and by curves, and indicate that the combined urea and ammonia N values of the saliva are normally between 6 and 13 mg. for each 100 cc. These combined values closely approx. those of the urea N of the blood. In urea retention the combined urea and ammonia N of saliva always increase with an increase in the blood urea N. The combined N of saliva is a valuable index of renal functional capacity. The detn. of the combined N of saliva may precede or replace blood urea N detns., especially in children and in other persons difficult to bleed. The finding of a normal combined N value in the saliva excludes the possibility of an abnormal blood-urea value. High combined N values in the saliva indicate the need of studies of the blood. L. W. RIGGS

Simultaneous variation in acidity of different portions of gastric contents. Its relation to fractional analysis. F. W. WHIRE. *J. Am. Med. Assoc.* 79, 1499-1503 (1922).—About 500 analyses of gastric contents for free and total acidity in 50 cases after an Ewald test breakfast were made by rapid (0.5 min.) and slow (15 to 20 min.) fractional methods. The position of the tube tip was located by the fluoroscope. The contents of the stomach at the end of 1 hr. is not usually in the form of a uniform mixt. The acidity of different fractions taken in rapid succession varies from 20 to 30 "points" or

more in 40% of the tests. A point is defined as $0.1 N \text{ NaOH} \times 10$. The max. simultaneous variation in acidity at the end of 1 hr. was 36 points of free HCl and 50 points of total acidity. The av. figures were 17 and 21, resp. This simultaneous variation was not due to a variable position of the tube tip in the stomach, or as a rule at the end of 1 hr. to variable duodenal regurgitation, but to very incomplete mixing of acid secretion with the contents of the stomach. This variation was partially overcome by artificial mixing of the contents of the stomach and by the use of water test meals. The simultaneous variation of fractions at the end of 1 hr. is often greater than the variation in the usual "fractional curve," beginning 1 hr. after the test breakfast and ending when the stomach is empty. While these limitations lessen the clinical use of fractional analysis, gastric analysis will be of value in the examn. of the fasting contents of the stomach, in the single 1 hr. test of secretion, in low secretion cases, in achylia and in testing the emptying time of the stomach.

L. W. RIGGS

Pathogenesis of parathyroid tetany. L. R. DRAGSTEDT. *J. Am. Med. Assoc.* 79, 1593-4 (1922).—Eleven adult dogs were fed a ration of boiled rice, beef heart and 50-100 g. of lactose each 24 hrs. for 5 days, when the thyroid and parathyroid glands were removed and the feeding was continued. Seven of the animals died after showing symptoms of tetany and 4 recovered. Fifteen adult dogs were fed a ration of white bread, milk and 50-75 g. of lactose per day for 10 to 14 days when the thyroid and parathyroid glands were removed. Eleven recovered from all symptoms of tetany. These and the 4 of the first group were in good health several months after the operation. Attempts to substitute the stock diet or one of meat for the bread, milk and lactose within 8 weeks resulted in more or less severe tetany. After about 6 weeks the stock diet could be used, but a heavy feeding of meat, especially if partly spoiled, or the occurrence of constipation would often precipitate an attack of tetany in an otherwise normal appearing dog. The mechanism of this readjustment of the body to the loss of the parathyroid glands after 5 or 6 weeks of dietary treatment has not yet been definitely determined. Parathyroid tetany or depression is due to an intoxication. The responsible toxic substances come chiefly from the gastro-intestinal tract. They arise through the activity of the proteolytic group of intestinal bacteria, and are probably for the most part protein-split products of the nature of amines. The function of the parathyroid glands is to prevent intoxication by these poisons. The parathyroid glands do not furnish a hormone necessary for life, and dogs may be kept alive indefinitely after their removal, if treatment directed to the prevention of this toxemia of intestinal origin is carried out.

L. W. RIGGS

The mechanism of the Ehrlich diazo reaction. III. LEO HERMANS. *Z. physiol. Chem.* 122, 98-103 (1922); cf. *C. A.* 16, 268.—A substance, supposed to be an oxidized coumarone of the formula $C_8H_6O_4$, was isolated from the urine of tuberculosis patients. It is the basis for the statement that "the Ehrlich diazo reaction depends upon the excretion of phenolic metabolism products and is to be regarded as an expression of toxic protein decomposition."

R. L. STEHLÉ

The unsaturated alcohols isolated from the fat of ovarian dermoid cysts. JOHANN MUCK. *Z. physiol. Chem.* 122, 125-42 (1922).—A Br deriv., $C_{11}H_{18}OBr$, was isolated. No ischolesterol or hydroxycholesterol was found. By oxidation an acid, $C_{11}H_{18}O_4$, giving well defined Ca, Ba and Ag salts was obtained.

R. L. S.

Insusceptibility to sensitization and anaphylactic shock. W. T. LONGCOPE. *J. Exptl. Med.* 36, 627-43 (1922).—Attempts to produce anaphylactic shock in white rats by 2nd intravenous or subdural injections of horse serum have failed. It was impossible to demonstrate either by skin reactions or by the uterine reaction that white rats can be sensitized to horse serum. It was also impossible to sensitize guinea pigs passively with the serum of white rats presumably immunized to horse serum. In spite of the

fact that the rat could not be made anaphylactic to horse serum the tissues of the animal reacted with the serum to form precipitins in fair concn. and the antigen disappeared from the circulation soon after the precipitins reached their greatest concn. in the blood. This would indicate that in the white rat anaphylaxis and precipitin formation are independent and represent different types of immunological processes. C. J. WEST

The action of sodium salicylate upon the formation of immune bodies. HOMER F. SWIFT. *J. Exptl. Med.* 36, 735-60(1922).—Rabbits treated with Na salicylate in daily doses of from 0.16 to 0.2 g. per kg. of body wt. and at the same time immunized with intravenous injections of *Streptococcus viridans*, both living and in the form of vaccines, and also with washed sheep red blood cells, showed diminished complement-fixing antibodies, agglutinins and hemolysins when compared with controls similarly immunized. If the antigens were treated with Na salicylate *in vitro* and subsequently injected intravenously into rabbits, the animals usually showed lower antibody curves than did rabbits that received the untreated antigen intravenously and Na salicylate by stomach tube. The beneficial effect of Na salicylate in rheumatic fever patients probably cannot be attributed to an increased production of circulating immune bodies against the infectious agent. This is, however, no contraindication to the administration of salicylates to patients suffering from infectious diseases. C. J. W.

H—PHARMACOLOGY

ALFRED N. RICHARDS

The medicinal use of protected metal hydrosols and the explanation of their behavior. II. J. VOIGT. *Kolloid Z.* 30, 243-9(1922); cf. C. A. 16, 293.—The color change of "Dispargen" red (Chem. Fabrik Reisholz) was observed both by transmitted and reflected light upon addn. of varying concns. of NaCl and NaNO₃, and the no. of Ag particles counted after each addn. of electrolyte so as to follow the course of the coagulation. Similar expts. were made with "Dispargen" green, using NaCl, NaNO₃, CaCl₂ and HCl. In this way it is shown that even a large excess of protective colloid will not prevent flocculation when too concd. electrolyte solns. are used. Results *in vitro*, however, must not be applied broadly to the case of intravenous injections of metal hydrosols. It is an important fact, that, for stability in acid protective colloid solns., a definite concn. of salts is required. In the case of NaCl this value is close to that of physiol. salt soln. Differences in salts, even of the same valence, point the way to further investigations, particularly in connection with the ultimate charge on the particles. In conclusion the point is emphasized that, owing to the extremely complicated constitution of protected metal hydrosols, it is a matter of the greatest difficulty to propose at present any theory as to their fate after intravenous injection into the warm-blooded organism. H. W. BANKS, 3RD.

Effect of magnesium sulfate on the secretion of bile. EMMETT B. FRAZER. *J. Am. Med. Assoc.* 79, 1594-6(1922).—Expts. on dogs were undertaken to det. whether MgSO₄ introduced directly into the duodenum or into the circulation would cause any change in the vol. or in the character of the bile. The numerical results of tests upon a large number of animals are assembled in 4 tables and illustrated by 4 charts of graphs. The results were entirely negative. In some instances the rate of flow was retarded. When bile was injected into the duodenum there was a definite and prompt increase in the flow of bile. L. W. RIGGS

The problem of deep X-ray therapy from a physical standpoint. FRIEDRICH DESSAUER. *Klin. Wochschr.* 1, 1395-7(1922).—A review. MILTON HANKE

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The detection of hypochlorites and chloramines in milk and cream. PHILLIP RUPP. U. S. Dept. Agr., *Bull.* 1114, 1-5(1922).—Available Cl such as that derived from hypochlorites and chloramines in milk and cream may be detected in aints. as low as 1 part in 50,000 by adding 1.5 cc. of a 7% KI soln. and 4 cc. of HCl (1:2) to 5 cc. of the milk or cream in a medium-sized test-tube. The latter with its contents is placed in a water bath, heated to 85°, allowed to remain for 10 min., cooled and 0.5 to 1 cc. of starch soln. added. The presence of Cl is indicated by the pale-yellow color of the liquid below the curd changing to a light-reddish purple, passing through red purple into a deep-blue purple as the amt. of Cl present is increased. Milk pasteurized, after the addition of hypochlorites, at 145° F. for 30 min. reacts the same as raw milk. W. H. R.

Autolysis of beef and mutton. W. R. FEARON AND D. L. FOSTER. *Biochem. J.* 16, 564-71(1922).—Beef cannot be frozen and thawed again without marked changes taking place in the appearance, palatability, and general physical state of the meat, while nothing of the sort happens when mutton is similarly treated. Examn. of the post-mortem autolysis of beef and mutton has thrown no light on their different behavior after being frozen. The processes in both are parallel, both at incubator and at low temps. In the case of mutton equil. is reached at a higher percentage of sol. N than in beef; but the initial non-coagulable N is higher, so that the curves are comparable. It is probable, therefore, that the differences in the 2 kinds of muscle are phys. rather than chem. perhaps due to the structure and phys. properties of the fibers. B. H.

Presumptive test for the etiologic factor in bacterial food poisoning. VICTOR BURKE AND C. W. MAY. *J. Am. Med. Assoc.* 79, 1669-74(1922).—The causes of food poisonings may be roughly classified into 4 groups as regards diagnosis: (1) bacterial toxins, (2) organisms of the paratyphoid enteritidis group, (3) ptomaines and naturally poisonous food such as toadstools, (4) chem. poisons such as poisonous metals. The test described consists of a rapid confirmed test for the presence and type of botulinus toxin combined with a presumptive test for members of the paratyphoid enteritidis group. For details the original paper should be consulted. L. W. RIGGS

Carob tree and carob beans. ROTHÉA. *Bull. sci. pharmacol.* 29, 443-9(1922).—A good bibliography. This article takes up the accidents that have followed carob bean administration, the parasites of the bean, adulteration, nutritive value and preservation. F. S. HAMMETT

Field experiments with sunflowers. L. G. LITTLE. *Agr. Gaz. N. S. Wales* 33, 622-24(1922).—Analyses are given of sunflowers and maize, showing that the former is about twice as high in albuminoids and other nitrogenous compds. as the latter.

W. HAZEN

The odorous constituents of apples. II. Evidence of the presence of geraniol (POWER AND CHESNUT) IID. Confirmation of the occurrence of linalyl esters in peaches (POWER AND CHESNUT) IID.

Milk mixture. P. G. KINZER. U. S. 1,432,699, Oct. 17. Cream is sepd. from fresh whole cow milk, the cream is churned to sep. the butter fat and the buttermilk thus obtained is mixed with the original skimmed milk and emulsified with a vegetable fat free from fatty acids, e. g., coconut oil.

Condensed milk mixture. C. S. STEVENS AND C. A. BAUMANN. U. S. 1,432,632, Oct. 17. Milk from which butter fat has been removed is emulsified with another fatty

substance, *e. g.*, coconut oil, and the mixt. is condensed or evapd. to a cream-like consistency. U. S. 1,432,633 relates to the prepn. of a similar product by addn. of a vegetable fat, such as coconut oil (free from fatty acids), in successive portions during evapn. to milk previously deprived of its natural butter fat content. U. S. 1,432,634 specifies addn. of a fat free from fatty acids, *e. g.*, coconut oil, heated to a temp. of about 33–37° (which is about the temp. at which the milk is maintained), to milk from which fat has previously been removed, with homogenizations preceding and following condensation of the mixt. U. S. 1,432,635 relates to prepn. of finely divided powdered milk product by evapn. of a nebulous spray of a stable emulsion formed of a vegetable fat such as coconut oil and milk deprived of its natural fat.

Condensing milk. G. GRINDRON. U. S. 1,432,686, Oct. 17. A relatively small portion of a total amt. of skimmed milk to be treated is condensed to the point of max. hydration of the colloids while maintaining a temp. below that which would cause coagulation of the albumin. This condensed portion is then homogenized with the cream previously sepd. from the milk; the albumin in the homogenized mixt. is coagulated and the product is mixed with the main portion of the skimmed milk which meanwhile has been separately condensed. The product is suitable for canning and sterilizing and treatment in the manner followed serves to avoid undesirable effects when extremely high pressures are employed in homogenization.

Treating grain, flour, meal, etc. NAAMLÖÖZE VENNOOTSCHAP INDUSTRIELLE MAATSCHAPPIJ VOORHEEN NOURY AND VAN DER LANDE. Brit. 186,571, Nov. 24, 1921. Addition to 102,967 (C. A. 11, 1219). Flour, meal, or other milling product or dough is treated with org. or inorg. peroxides during, before or after grinding, and the mixt. is allowed to stand so that enzymes contained in the flour, etc., may decompose the peroxide. Enzymes obtained from germ of wheat, maize, etc., and moisture or certain chem. substances, such as CaSO_4 , acids, acid salts, etc. which increase the action of the enzymes, may be added. Light or actinic rays or heat may be applied simultaneously. The warm moist air of the mill may be utilized to complete the bleaching by the time the flour leaves the mill.

Shortening for foods. H. V. DUNHAM. U. S. 1,432,057, Oct. 17. Uncooked flour or similar material contg. unbroken starch granules is mixed with sufficient H_2O to form a fluid mass, mixed with an edible oil, *e. g.*, coconut oil in amt. to constitute 20–70% of the final product, homogenized at a temp. below that which would break the starch granules and then dried at a similarly low temp. to obtain a powder which can be sifted.

Shortening for foods. H. V. DUNHAM. U. S. 1,431,938, Oct. 17. Wheat flour or a similar starchy material is boiled in H_2O and emulsified with coconut oil or other normally solid edible fatty oil. The emulsion is then homogenized and dried.

Casein and oil mixture. H. V. DUNHAM. U. S. 1,431,937, Oct. 17. See Brit. 169,276 (C. A. 16, 847).

Odorless and colorless soy-bean flour. Y. YAMAMOTO. U. S. 1,433,168, Oct. 24. Coarsely pulverized soy-bean material is treated with a very dil. aq. soln. of HOAc to remove odorous and coloring substances, the mass is dried, oil is extd. from it and it is then ground to produce a flour adapted for use in foods, soap or washing powders.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

The colloid mill. A. FORSTER AND J. REILLY. *J. Soc. Chem. Ind.* 41, 435–8R (1922); cf. C. A. 16, 450; 2 cuts.—Plauson has modified the “dismembrator” in which

the material in aq. suspension is fed on to the axis of a high speed revolving arm-wheel, surrounded by a number of close-fitting baffles and built a standard size 15-liter mill, running at 8000 r. p. m. Larger sizes have been built. Many substances are dispersed in the mill so rapidly as to be capable of being run continuously through at a comparatively rapid rate. With more resistant materials it is proposed to make the process continuous by the use of a number of mills in series. Industrial uses claimed for this mill have been divided into 4 groups: (1) Prepn. of plastics from sawdust, china clay, slag, shale residues, rubber waste, gelatin, etc. (2) Prepn. of colloidal solns. from S, creosote, Cu, Mn, and Ag for use in disinfectants and sprays; phosphate feldspar for fertilizers; tar asphalt for road sprays; mineral and organic pigments for inks; graphite, oil and H_2O for lubricants; resin for polishes; resin, cellulose esters, copal, bakelite and rubber for enamels, etc.; metals, alloys and ultramarine for paints. (3) Division of materials for chem. action, e. g., fats for cold saponification; nitro compds. for cold reduction; Ni for hardening oils; peat and cellulose for fermentation. (4) Sepn. of mixts. by fractional disintegration, e. g., metallic ores from rock; kaolin from silica; shales; dyes, etc.

H. M. McLAUGHLIN

Industrial methods of liquefaction and practical applications of low temperatures. K. S. MURRAY. *Trans. Faraday Soc.* (advance proof) 1922.—M. discusses sep'n. of air constituents with special reference to low temp. liquefaction, describing and illustrating the essential features of the Linde and Claude systems. Linde obtains the Joule-Thomson cooling effect, rendering it cumulative by means of the counter-current heat interchanger. The temp. gradient depends upon the difference between the b. p. of N and O. O losses in rectification in this process may reach $\frac{1}{2}$ of the O in the air. The outstanding features of Claude plants are (1) cooling by means of an expansion engine, (2) a selective system of rectification effected by partial sep'n. of O and N, (3) a combined system of heat interchange and drying which renders chem. abstraction of moisture from the air unnecessary. The operation of both processes are completely outlined. Cheap O requires large liquid air units worked to their full capacity. The Jeffries Norton process, while clever and original, is generally regarded somewhat impractical.

W. H. BOYNTON

The Krause process. SIEGENS. *Z. angew. Chem.* 35, 533-5(1922).—In the Krause process the liquid is sprayed into the drying chamber by a horizontal rotating disk. Many substances which would clog a spray nozzle can be handled in this way. If the speed of the disc is high enough, the drying is so rapid that many materials can be dried which cannot be handled by any other process. It is claimed that a milk powder can be made which, when emulsified in water, cannot be told from fresh milk. Other processes suggested are the drying of colloidal solns., exts. of drugs, active principles of glands, dye wood exts., food solns. of all kinds, glue and gelatin, etc. Suspensions can be handled, and an interesting application is the drying of fine powd. coal suspended in NH_4NO_3 soln., the product to be used as an explosive. The process is covered by basic patent, Ger. pat. 297,388, 1912 and other further patents.

W. L. BADGER

Some materials of low thermal conductivity. EZER GRIFFITHS. *Trans. Faraday Soc.* (advance proof) 1922.—Expanded rubber, balsa wood, fibers of wood, *Kängia Australia*, eel grass mats, and compressed peat (treated and untreated) were examined as to their values as insulating materials. In a granular form expanded rubber has about twice the insulating efficiency of granulated cork and about four times that of slab cork. Its soft variety varies in density from 0.059 to 0.12 C. G. S. units (8.7-7.5 lbs./cu. ft.) while a hard variety resembling ebonite has a density of 0.17 (10.6 lbs./cu. ft.). Balsa wood is probably the lightest wood known. It may be worked with wood-working tools operating at high speed, and while subject to decay may be rendered

waterproof by means of preservatives. The heavy wt. of compressed peat is a disadvantage. As the thermal conductivity of insulating materials is not an invariable const., it is advisable to test samples of consignments as fuels are tested for calorific values.

W. H. BOYNTON

Heat transfer by conduction and convection. II. Liquids flowing through pipes. W. H. MCADAMS AND T. H. FROST. *J. Ind. Eng. Chem.* **14**, 1101-5(1922); cf. *C. A.* **16**, 3351.—By dimensional reasoning it has been shown that the coeff. of heat transfer from a metal wall to a liquid inside a pipe should be a function of $Du\rho/\eta$, where D is the inside pipe diam. in in., u = av. liquid velocity in ft. per sec., ρ = density in lbs. per cu. ft., and η = relative viscosity of the liquid film in centipoises. Data from Clement and Garland, Webster, and 4 undergraduate theses are plotted and show a very good agreement. The equation suggested is $H_1 = (22.6 K/D) (Du\rho/\eta)^{0.8}$, where H_1 is the thermal cond. from metal to liquid in B. t. u. per sq. ft. per °F. per hr., K is the mean thermal cond. of the liquid film in B. t. u. per sq. ft. per °F., per ft. per hr., and the other symbols as above.

W. L. BADGER

Lubricating oils, journal friction and friction experiments. DUFFING. *Z. angew. Chem.* **35**, 605-7(1922).—D. describes an oil testing machine of the Thurston type, by means of which the coeff. of friction of an oil may be tested in a bearing under a measured load.

EUGENE C. BINGHAM

New methods of physical measurements for the valuation of lubricants. VIEWEG. *Braunkohle* **21**, 454-5(1922).—Ordinary oil tests are unsatisfactory for detg. lubricating values because they show neither the thickness of the film nor the displacement of the mech. alignment. Two methods are given for the measurement of the thickness of films. (1) On the front surface of the journal of a shafting is drawn a cross-hatched lattice with lines 0.002 mm. apart. On rotation, the point of intersection of the axis of the shaft with the plane of the lattice appears as a fine point. The displacement of this point is measured by a microscope with ocular micrometer. This is usually 0-0.1 mm. (2) The displacement of the shaft is measured both transversely and longitudinally by a photomicrographic method with a collimator, the optical axis being tangential to the shaft. Considerable differences in displacement were found for various types of lubricants.

C. C. DAVIS

The significance of the temperature coefficient of viscosity for judging oils. HANS VOGEL. *Z. angew. Chem.* **35**, 561-3(1922).—Viscosities should be measured at several temps. and expressed in abs. units (centipoises). The viscosity may be best represented by the formula: $\eta = \eta_{\infty}^{(t-t_{\infty})/(t-t_0)}$, where t_{∞} is the temp. at which $\eta = \infty$ and t_0 is the temp. at which the viscosity is equal to that of water at 20.2°, i. e., 1 cp. Plotting $\log \eta$ against $\log t$ there is found a hyperbolic relationship and the greater the value of $t_{\infty} + t_0$, the flatter the curve. The flatter the curve, the less will be the friction in bearings running at low temps., the greater the assurance against rupture of the oil film at high temps., and the nearer may one approach the min. friction in a bearing without danger. Of the oils tested by V. in a modified Ostwald viscosimeter, "Volto" oils prepd. by a special process of elec. polymerization gave the most satisfactory curves.

EUGENE C. BINGHAM

The electric insulator industry. A. BÜLTMANN. *Z. angew. Chem.* **34**, 565-8, 573-8(1921).—B. reviews the various kinds of material commonly used for insulation in the elec. industry, and compares their value under different conditions. Photographic records of arcs under varying conditions are given.

W. E. RUDER

Effect of heat on the electric strength of some commercial insulating materials. W. S. FLIGHT. *J. Inst. Elec. Eng.* **60**, 218-35(1922); *J. Soc. Chem. Ind.* **41**, 222A.—Tests were made on flat sheets, or cylinders, of not less than 8" diam., in oil, dry air, and damp air. The temp. was varied from 30° to 100°. Papers, mica products, varnished

paper and cloth, fiber, wood, molded compn., etc., were tested. The results showed that elec. strength at 100° decreased for all materials tested, over that at 30° and that the decrease varied from 15% to 78% with different materials. Insulating materials should be tested at 100° rather than at normal air temp.

W. E. RUDER

Properties of electrical insulating materials of the laminated phenol-methylene type. J. H. DELLINGER AND J. L. PRESTON. *Bur. Standards, Tech. Papers No. 216*, 501-627(1922).—Data are given on the characteristics of bakelite, condensite, and formica.

T. S. CARSWELL

Application of electric service to the chemical industry. WM. B. TODD. *Chem. Met. Eng.* 27, 552-4(1922).—Applications of elec. service to the chem. industry are for motor drives, illumination, heating, transportation, electrolysis, elec. pptn., miscellaneous lab. uses and welding. For motor drives strict attention to type, size, and installation of motors is essential. Special precaution must be taken to protect motor windings against acid and other chem. fumes. For illumination purposes the chief considerations are elimination of the glare causing fatigue and injury to the eyes, and guarding against explosion risks.

LOUIS JORDAN

Ethyl chloride. C. F. JENKIN. *Trans. Faraday Soc.* (advance proof) 1922.—The phys. and chem. properties of C_2H_5Cl indicate its value as a refrigerant. Its crit. point is 190° and 54 atm. Its inflammability is its worst drawback. Impure C_2H_5Cl is satisfactory for refrigeration because the small proportion of CH_3Cl present raises the vapor pressure. Also in *Chem. News* 125, 249-51(1922).

W. H. BOYNTON

A rapid and accurate method for the calibration of storage tanks. J. W. M'DAVID. *J. Soc. Chem. Ind.* 41, 295-6T(1922); 1 cut.—The principle underlying the method is that water, flowing through a tube or orifice under a const. head, gives a const. rate of flow. From the time required to fill a given vessel, its total vol. can be calcd. If, however, the vol. per inch of depth is required, as in the case of non-cylindrical vessels, the flow must be stopped after a known interval of time, and the depth of liquid measured. The calibrator consists of a brass cylinder, 4" in diam. and $2\frac{1}{2}$ " long, fitted with a $\frac{3}{4}$ " overflow pipe, and a series of five nozzles to vary the rate of efflux. The outflow pipe of the same size extends, inside the calibrator, up to within $\frac{5}{16}$ " of the upper extremity of the overflow pipe. A perforated brass plate serves the double purpose of forming a support for the pipes and of reducing turbulence at the surface of the water. The calibration of the nozzles was reproducible to 0.3%. Since an increase in rate of overflow produces an increase of head, this source of error was investigated, and it was found that an increase of head of 0.1 inch increases the rate of outflow by 0.1%. A table is given showing the effect of temperature on rate of flow for the various nozzles. A practical test of this calibrator on a cylindrical acid tank, a 200-gal. stoneware tank, and an egg-ended boiler, for vol. per inch in the last case, showed it capable of giving results accurate to within 0.2%. With the largest nozzle, a 600-cu.-ft.-boiler can be calibrated in a little over 6 hrs., while with the $\frac{1}{4}$ " nozzle, small vessels such as nitrating pans require less than 10 mins. The entire app. weighs only 26 lbs. making it easily portable by one person.

T. F. BUEHRER

Purifying liquids. R. H. L. PENNELL. *Brit.* 185,798, May 11, 1921. H_2O or other liquid, before a final downward filtration through sand or sterilization by Cl, is given a preliminary filtration upward through chambers of successively greater area, so that the rate of flow is successively decreased. A suitable construction is specified.

Separating gaseous and liquid mixtures. C. METZGER AND E. LUETSCHEN. *Brit.* 186,027, Dec. 30, 1921. A gaseous or a liquid mixt. is sepd. by imparting to it a high velocity while splitting it, at the same time, into "individual fine threads" by mechanical

means. The threads are directed against an intermediate wall against which, from the opposite side, a material impinges or around which a material flows which takes up the heat inherent in the threads.

Oil emulsions. PLAUSON'S (PARENT Co.), LTD. Brit. 185,779, April 6, 1921. Oils, particularly mineral and tar oils, are subjected to a high-speed disintegration in a colloid mill in presence of H_2O and of an insol. mineral solid, *e. g.*, colloidal graphite, calcined MgO , or $MgCO_3$. Talc or graphite may be added to increase the consistency of the product. Pastes are obtained when not more than 6 parts of H_2O to 1 part of oil are employed; liquid emulsions when the H_2O exceeds this proportion. The products are suitable for use as lubricants.

Insulating composition. W. H. KEMPTON. U. S. 1,431,962, Oct. 17. Waterproof articles adapted for use in sheet form are formed of asbestos, portland cement and the reaction products of linseed oil and an oxidizing drier such as Mn resinate.

Heat insulation. H. MOCK. U. S. 1,433,088, Oct. 24. Heat-insulating bricks are formed with a core of powd. S and a surface layer of asphaltum.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

Flash evaporator furnishes pure make-up water to boiler. ANON. *Power Plant Eng.* 26, 1078-9(1922).—Raw water is heated under pressure in a tubular heater to a point below which impurities are deposited as scale. The heated water is pumped into a vacuum evaporator and immediately flashes into steam; the distillate is practically pure water claimed to be free from dissolved and entrained O. G. C. BAKER

Distilled water for boiler feed. ANON. *Power Plant Eng.* 26, 1013-4(1922).—Multiple heating effects are recommended for the production of distd. water for boiler feed. G. C. BAKER

De-aerating heater reduces tube corrosion. ANON. *Power Plant Eng.* 26, 1068(1922).—The water to be de-aerated is sprayed over trays and then falls into a storage pool in a vacuum heater. The steam used for heating the water is introduced through a perforated manifold at the bottom of the storage space, carries out the dissolved gases, and is withdrawn by an air pump. The vacuum maintained depends upon the final temp. to which the water is heated. G. C. BAKER

Typhoid fever and water supply. LANGDON PEARSE AND S. L. TOLMAN. *Public Works* 53, 226(1922).—A review of conditions around the Great Lakes. LANGDON PEARSE

Cemeteries and ground water supplies. ANON. *Dept. Public Health Mass.* 1920; *Public Works* 53, 230(1922).—Where free CO_2 is less than 17 p. m. corrosion of water pipes need not be feared. CO_2 in ground water is increased by cemeteries. L. P.

Annual report, Rivers Department, City of Manchester, for year ending March 29, 1922. F. J. WEST.—Part I deals with the work in connection with the maintenance of rivers and streams and the inspection and control of the manufacturers' trade refuse discharged into city sewers, part II with the administration of sewage works. Descriptions of the plants, vol. of sewage treated, methods of treatment used, methods of sludge disposal, costs, analytical data, etc., with extensive tables, are included. During the year research work upon the dewatering of activated sludge has been extended. Additions of light mineral matter such as fine dust materially assists the release of water from the sludge with the production of a cake of reduced water content. The availability of the N for plant food is unimpaired. The amt. of inert mineral matter required to pro-

duce a cake of 65–70% in 6 hrs. is so large as seriously to depreciate the value of the final product. In vacuum treatment preliminary treatment with acid facilitates the removal of water, and the cost is more than counterbalanced by the increased output. An 84–87% sludge or a reduction of vol. of sludge from 6 to 1 is obtained; preliminary heating does not seem practical—thin films at high rate are better than thicker films at a lower rate. It was possible to remove without vacuum entraneous water by (a) a slowly rotating wire-mesh cone fed internally or (b) a revolving gauze cylinder in the sludge itself. An av. of 94% H₂O and a reduction vol. of 3 to 1 is obtained. On passing this product over an endless wire gauze carried on rollers over which travelled a superimposed gauze or impervious band in such a manner as to have a pronounced squeezing effect the H₂O content was further reduced to 86%. Flotation expts. by impregnating the sludge with gas to lift the solid matter to the surface did not give promise. G. C. B.

Report of the Institute of Hygiene of Water on the salt content of the Weser at Bremen. K. THUMEN. *Mitt. Landersanstalt Wasserhyg.* 26(1921); *Gesundh. Ing.*, 128 (Mar. 11, 1922); *German Office Intern. Hyg. Publ.* 14, 981(1922); *Pub. Health Eng. Abstr.* (Dec. 9, 1922).—The permissible limits for the Cl content of water supplies are discussed. A former commission stated "an increase in Cl content of the Weser water to 350 mg. per l. at Bremen would not cause objection from a hygienic standpoint," while the National Inst. of Water Hyg. had already fixed the maximum at 170 mg. per l. Recent expts. showed water Cl content of 143 mg. per l. was judged "normal" by taste, but 190 mg. per l. had a salty or bitter taste. An allowance of 350 mg. per l. is protested against. G. C. BAKER

Atmospheric dust. J. S. OWENS. *J. Soc. Chem. Ind.* 41, 438–43R(1922).—The instrument for measuring atm. dust (*C. A.* 16, 777) was so arranged that a reduction of pressure and temp. caused, by impressing a very high velocity on the air in a ribbon-shaped jet 1 cm. long and 1 mm. thick, a condensation of moisture around the dust particles which were then deposited on a microscope cover-glass placed 1 mm. from the opening. This deposit could be examd. microscopically or microchemically and the number of dust particles counted. Some practical uses suggested for the instrument are: (1) to establish from the standpoint of health permissible standards of dust pollution; (2) to det. the relation between visibility of air and dust pollution; (3) to test the efficiency of air-purifying plants. H. M. McLAUGHLIN

Purifying liquids (Brit. pat. 185,798) 13.

Device for cooling, filtering and aerating water. O. P. BARNES. U. S. 1,432,522, Oct. 17.

Filter and settling chamber for water. J. G. ELLIS. U. S. 1,433,357, Oct. 24.

Filter for boiler feed water. F. L. MCGAHAN. U. S. 1,432,351, Oct. 17. Liquid is passed successively through adjacent chambers containing, resp., crushed Cu glance, charcoal and crushed lime-rock, in order to avoid incrustation of locomotive or other boilers.

Apparatus for distilling feed water for steam boilers. H. BALCKE. U. S. 1,432,521, Oct. 17. Vapor from a vaporizer is compressed and utilized as a heating medium.

Apparatus for separating suspended solids from sewage or other effluents. L. LINDEN. U. S. 1,432,766, Oct. 24.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Absorption by colloidal and noncolloidal soil constituents. M. S. ANDERSON, W. H. FRY, P. L. GILB, H. E. MIDDLETON AND W. O. ROBINSON. U. S. Dept. Agr., *Bull.* 1122, 1-20(1922).—A complete sepn. of the colloidal matter from the finer mineral particles of the soil was not found possible and a direct detn. could therefore not be made of the relative absorption in soils due to colloids and noncolloids from a fractionation of the soil into these 2 classes of materials. From a study of the absorptive capacities of 21 soil minerals powdered to definite sizes varying between 1 and 50 microns in diam., it was calcd. that except in the case of the most highly micaceous soils in which the noncolloidal absorptions might reach 10-20% of the whole soil absorption, less than 5% of the total absorption of the soil is due to the noncolloidal part. Absorption by noncolloidal constituents should therefore not seriously affect absorptive methods for detg. the amt. of colloids in soil. Minerals ground to a state of subdivision probably equal to that of the mixed soil colloids, or "ultra clays," absorb less than the av. ultra clay. The av. absorption of peat and synthetic inorg. gels, on the other hand, is more nearly like that of the ultra clays. The fact that soil colloids are not merely finely comminuted minerals but appear to be of quite different nature from the noncolloidal particles thus affords an explanation for the marked difference in the absorptive capacities of these 2 classes of soil materials. W. H. ROSS

A study of the influence of the lime-magnesia ratio on soils under continuous cultivation. H. H. HILL. Virginia Agr. Expt. Sta., *Tech. Bull.* 24, 15(1922).—Working with Hagerstown loam soil lime produced greater yields over a 14-year period than mineral fertilizers. Continuous cropping with corn has changed the proportion of Ca to Mg in the soil from about 1 to 1, to a relation of 1 of Ca to 2 of Mg. Good results were obtained with a proportion of 1 of Mg to 1 of Ca. When Mg was in excess crop exhaustion was manifest. When acid phosphate was used alone the Ca-Mg ratio was not as wide as on the plots which received mixtures of acid phosphate, K_2SO_4 and $NaNO_3$. The narrowing of the ratio between Ca and Mg is thought to be due to the Ca in combination with the acid phosphate. K_2SO_4 and $NaNO_3$ when applied alone exerted no appreciable effect on the retention of Ca. A review and discussion is given.

J. J. SKINNER

The soils of the Murrumbidgee Irrigation areas. H. J. BRAUND. *Agr. Gaz. N. S. Wales* 33, 631-33(1922).—A discussion. Recommendations for improvement are made. Application of gypsum is beneficial. W. HAZEN

The reaction of soils in the field as influenced by the long continued use of fertilizer chemicals. PAUL S. BURGESS. Rhode Island Agr. Expt. Sta., *Bull.* 139, 33 (1922).—Detns. of acidity by the H-ion electrometric method and the Jones lime requirement method were made on soil from a number of plots in fertilizer expts. on Miami silt loam. The plots have been fertilized similarly each year for a long period. It was found that Thomas slag, acid phosphate, ground bone, floats and double superphosphate tend to reduce soil acidity as compared with no P. Finely ground starfish and $NaNO_3$ reduced acidity decidedly, while horn meal, dried blood, acid fish, hoof meal, tankage and hen manure slightly increased it. $(NH_4)_2SO_4$ greatly increased soil acidity. K_2CO_3 , KCl, K_2SO_4 and manure salts reduced soil acidity as compared with no K. Kainite was most active in this respect, followed by double manure salt, KCl and K_2SO_4 . Carbonates of Na and K greatly reduced acidity in comparison with chlorides. Non-leguminous green manure crops annually turned under for long periods slightly decreased soil acidity while leguminous cover crops similarly incorporated with soils tend to increase soil acidity. J. J. SKINNER

The phosphoric acid content of liquid manure. E. DEUSSSEN. *Chem.-Ztg.* 46, 876-7 (1922).—Coal-briquet ashes were not effective as agents for the removal of P_2O_5 from liquid manure. Repeated centrifuging reduced the P_2O_5 content of liquid manure from 0.24 to about 0.04%. The original liquid manure contained more than enough Ca and Mg completely to ppt. all the P_2O_5 present. D. concludes that the dissolved P_2O_5 is present as the phosphates of Ca and Mg in the colloidal form. The addition of heavy excesses of $CaCl_2$ or $MgSO_4$ removed the last traces of P_2O_5 from soln.

K. D. JACOB

Storage experiments with lime intended for sprays. A. A. RAMSAY. *Agr. Gaz. N. S. Wales* 33, 747-9 (1922).—Gives analyses of lime which had been kept under water for different periods of time.

W. HAZEN

Fertilizers. A. L. KRISS. *Brit.* 186,035, July 18, 1922. Phosphate rock is fed into a heated drier contg. a soln. of one or more alkali metal salts, e. g., Na_2SO_4 , Na_2CO_3 , K_2CO_3 , a mixt. of Na and K sulfates, and a mixt. of Na_2CO_3 , Na_2SO_4 and K_2CO_3 at 500-1072°. A suitable construction is specified.

Treating phosphates. EISENWERK GES. MAXIMILIANSSTÜTTE. *Brit.* 186,223, Aug. 9, 1921. Phosphoric compds. suitable for fertilizers are made sol. in citric acid and partly sol. in citrates by intimate grinding with about 1-1½ parts of sulfate, chloride, silicate or nitrate of the alkali or alk.-earth metals, NH_4 , or Mg. Double salts of the alkali metals and Mg also may be used. Cf. 6429, 1906 and 151,024.

16—THE FERMENTATION INDUSTRIES

C. N. FREY

Development of a wild yeast into a yeast having good fermenting capacity and suitable baking strength. H. HAEHN. *Z. Spiritusind.* 45, 231-2, 237-8, 251, 268, 275, 287 (1922).—A *Torula* yeast (Fodder yeast) of low fermenting activity but high reproductive power was developed into a yeast suitable for bread-making. This was accomplished by growing successive generations in a high concentration wort and aerating very gently. The original *Torula* yeast had a fermenting capacity of 202 cc. CO_2 in 2 hrs., (10 g. yeast, 40 g. sugar, 400 cc. H_2O), and it was developed to give 665 cc., which is equivalent to that of a good baking yeast. Baking tests also indicated that the yeast was equal to good bakers' yeast for bread-making. The development of fermenting activity depends on being able to stimulate the production of zymase or to activate it. Possibly both activators and zymase are produced in larger quantities. Zymase does not exist in the cells in the free state, but combined with the protoplasm. C. N. F.

Process for the production of industrial absolute alcohol and its application to the preparation of a domestic motor fuel (MAKILLER AND VAN RUYMBEKE) 21.

Low-alcoholic beer. M. STAGL. U. S. 1,432,422, Oct. 17. A "standard beer" is dild. with a low-alc. fermented brew in such proportions that the alc. content of the mixt. is reduced to the desired degree. Sufficient free lactic acid is provided in the constituents to give the mixt. a free acid content of about 0.05%.

Treating malt. C. F. HYDG. *Brit.* 186,161, June 22, 1921. The coarse meal and grits obtained by crushing malt for brewing purposes are sepd. from the fine meal and are mashed to render the starch sol., after which the mash may be used as mashing-liquor for the remainder of the ground malt, or the latter may be doughed into it. A suitable construction is specified.

Fatty acids; carbonic acid; hydrogen. LEFRANC ET CIE. Brit. 186,572, Feb. 2, 1922. Waste cellulosic materials such as wood waste are hydrolyzed to impure sugary worts, which, after purification, are subjected to symbiotic bacterial fermentation to produce fatty acids, mainly butyric acid. The hydrolysis of the disintegrated wood waste is effected by means of dil. H_2SO_4 and superheated steam; the acid liquors are then neutralized with lime or chalk; the sugar soln. is extd. from the product by exhaustion, and purified from gums, resins, mucilages, etc., by adding excess of milk of lime, followed if necessary by passage of the decanted soln. through animal charcoal. The purified wood wort is then treated with the ferments obtained by inoculating sugar solns. contg. mineral salts with bacilli of the intestinal digestion of herbivora or contained in garden earth; by this means, all the reducible sugars of the wood wort are converted into acids, viz., butyric, acetic, propionic, valeric, and caproic acids. The fermented wort is concd. to a sirup, preferably *in vacuo*, and treated in a still with H_2SO_4 or HCl or preferably NaHSO_4 to liberate the free org. acids which distil off and are fractionally sepd. The CO_2 of the fermentation is recovered by absorption in Na_2CO_3 , from which it is freed by boiling; the H_2 also may be collected.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Iodine determination in ferrous iodide pills. I. M. KOLTHOFF. *Pharm. Weekblad* 59, 1100-3(1922); cf. *C. A.* 16, 4006.—The following method has the advantage of greater simplicity and rapidity. Triturate 10 pills with H_2O in a mortar and rinse into a 100 cc. volumetric flask. Add 2-5 cc. 0.1 *N* $\text{Na}_2\text{S}_2\text{O}_3$ and 20 cc. 0.2 *N* $\text{Ba}(\text{OH})_2$. The reaction should be alk. to litmus. Dil. to 100 cc., allow the ppt. to settle and filter. To 10 cc. of the filtrate add 5-10 cc. 4 *N* H_3PO_4 , then freshly prepd. $\text{Ca}(\text{OCl})_2$. A sepn. of I first occurs, and this is then oxidized to HIO_3 . Add more $\text{Ca}(\text{OCl})_2$ and 100 cc. H_2O . Boil off the excess of Cl , cool, add 5 cc. *N* KI , and titrate with 0.1 *N* $\text{Na}_2\text{S}_2\text{O}_3$. 1 cc. of the latter = 2.11 mg. I per pill.

A. W. DOX

Contributions to the knowledge of *Terebinthina laricina*. L. E. GOESTER AND R. P. C. FRANSSEN. *Pharm. Weekblad* 59, 1154-60(1922).—The assay of *Terebinthina laricina*, the balsam from *Larix europaea*, consists according to the Dutch Pharmacopeia in the detn. of 2 acid numbers, the 1st by direct titration of the alc. soln., and the 2nd by titrating back after boiling 1 hr. with excess of alkali. The 1st represents free resin acids, and the 2nd was formerly supposed to correspond to the sapon. number of esters. The authors show that the 2nd is due to the presence of an acetyl deriv. which on treatment with alkali yields AcOH and a cryst. substance m. 100.5°.

A. W. DOX

Apparatus for putting sterilized serums and enzymes in ampules. SCHERKMESSER. *Chem.-Zig.* 46, 973-4(1922).

J. H. MOORE

Preparation of sulfarsphenamine. CARL VOEGTLIN AND J. M. JOHNSON. *J. Am. Chem. Soc.* 44, 2573-7(1922).—By treating arsphenamine in H_2O with 2 mols. HCHO and then with 4 mols. NaHSO_4 under definite conditions there is obtained a substance, designated *sulfarsphenamine (A)*, which, while not a pure chem. compd., is fairly uniform in As and S content and in biol. behavior. From its method of prepn. and the compn. of the free acid (which seps. with 3-4 mols. H_2O), *A* seems to consist chiefly of the compd. $[\text{4,3-HO}(\text{NaO}_2\text{SOCH}_2\text{NH})\text{C}_6\text{H}_4\text{As}]_n$. It does not reduce indigo carmine, unless previously treated with Zn and AcOH , and can thus be distinguished from neoarsphenamine. Extensive animal experimentation, the results of which will be published elsewhere, has shown that *A* is suitable for subcutaneous injection and is very effective in the treatment of protozoal diseases; moreover, its aq. solns. are remarkably stable and do not increase in toxicity on standing in the air for 24 hrs.

C. A. R.

Examination of neoarsphenamine. II. Constitution of the French drugs. A. D. MACALLUM. *J. Am. Chem. Soc.* **44**, 2578-82(1922); cf. *C. A.* **15**, 1715.—The French products consist entirely of doubly substituted arsphenamines; their most noticeable physical characteristic is that they dissolve without change in weakly acid as well as in neutral and alk. media; they decomp. at relatively higher temps. than the neoarsphenamines, are less affected by atm. O and are of lower toxicity but also of lower trypanocidal activity. The iodometric method described in the 1st paper has been extended for analysis of the methylene-bisulfite group, which appears to rank in importance with the sulfoxylate group in these preps.; the development consists essentially in making use of the oxidation figures obtained when a prepn. is treated with I successively in acid and alk. soln. and from these deriving the group configuration by the aid of elementary analyses. Below are the relative As %, curative dose (g. per kg.) and tolerated dose, resp., of typical com. samples, as detd. on mice infected with *Trypanosoma equiperdum*: arsphenamines 30, 0.0075-0.0125, 0.15-0.19; Na arsphenamines 20, 0.015-0.025, 0.25-0.3; neoarsphenamines 20, 0.0225-0.04, 0.3-0.4; French neo mixts. 20, 0.04-0.06, 0.4-0.5. C. A. R.

Adams' Wonder Capsules. ANON. *J. Am. Med. Assoc.* **79**, 1867(1922).—Each capsule contained about 5 grains of a white, cryst., coarsely granular powder, identified as benzyl succinate. L. E. WARREN

A reinvestigation of the proximate composition of Rhamnus frangula. J. A. GUNTON AND GEO. D. BEAL. *J. Am. Pharm. Assoc.* **11**, 669-82(1922).—The purpose was to det. whether the anthraquinone derivs. in frangula are present in the free state or in combination, possibly as glucosides. The drug (from France) contained H₂O 6.01, ash 5.75, N 0.74, protein (N × 6.25) 4.62 and HCN 0.005%. The ash had a greenish cast suggesting Mn. This was found and the amt. detd. in frangula (a), cascara (b) and rhubarb (c). The values were for (a) 0.0084, (b) 0.0402 and (c) 0.0223%. No relationship between Mn content and purgative value is apparent. On heating short of combustion a yellow brown sublimate was produced which contained a few microscopic crystals and which gave a reddish brown color with alkalis. Alkaloids were absent. A portion of the drug was extd. successively with petr. ether, Et₂O, CHCl₃, EtOAc and 95% EtOH. The extractives obtained were petr. ether 3.8, Et₂O 2.3, CHCl₃ 4.8, EtOAc 6.8 and EtOH 36.0%. For the detn. of free hydroxyanthraquinones 5 g. of the finely ground drug (previously dried at 70°) were weighed with 200 cc. of CHCl₃. The mixt. was heated in a reflux app. for 15 min., the mixt. cooled, the solvent decanted through a filter and the residue washed with CHCl₃. The CHCl₃ soln. was shaken repeatedly with 5% NaOH, the alk. exts. were shaken with CHCl₃ to remove emulsified fats, the soln. acidified with HCl and the liberated anthraquinone extd. with CHCl₃. The soln. was filtered, evapd., the residue dried at 100° and weighed. For combined hydroxyanthraquinones the residual drug from the first extns. was returned to the reflux app., CHCl₃ added to the previous wt., 50 cc. of 25% H₂SO₄ added, and the mixt. heated at the b. p. of CHCl₃ for 2½ hrs. The cooled mixt. was made up to the original wt. with CHCl₃; 150 cc. of the filtered CHCl₃ portion were shaken with 50 cc. of 10% NaHSO₄ soln. The CHCl₃ was then shaken with 100 cc. of 1% HCl, the CHCl₃ evapd. and the residue weighed. Several drugs were assayed by this method and the result in free (a), combined (b) and total (c) hydroxyanthraquinones compared. *Frangula* (a) 1.14, (b) 2.63 and (c) 3.77%. *Frangula* (Am. grown) (a) 0.87, (b) 3.39 and (c) 4.26%. *Cascara* (a) 1.11, (b) 2.70 and (c) 3.81%. *Rhubarb* (a) 0.29, (b) 2.32 and (c) 2.61%. *Rumex crispus* (a) 0.72, (b) 1.18 and (c) 1.90%. *Rumex ecklonianus* (from S. Africa) (a) 0.26, (b) 1.36 and (c) 1.62%. Cold H₂O removed 18% of a bitter ext. which contained hydroxyanthraquinones and reducing sugars. Ash from H₂O ext. 0.80% (of wt. of bark). CHCl₃ ext. from H₂O ext. 0.56% (of wt. of bark). The action of emulsin

increased the CHCl_3 ext. from the H_2O ext. Hot H_2O extd. 36.80%, the ash of which amounted to 1.95% (of the wt. of bark), CHCl_3 ext. 2.40%. Pentose was present in addn. to the constituents in the cold H_2O ext. An ext. was prepd. by exhausting the drug with 95% EtOH and concg. in partial vacuum. The residue was mixed with purified sawdust and dried. The mixt. was extd. successively with petr. ether, 8% $(\text{NH}_4)_2\text{CO}_3$, Et₂O, $\text{C}_6\text{H}_5\text{OH}$, 5% Na_2CO_3 , 2% NaOH, 50% EtOH and the fractions were submitted to various treatments. The substances isolated and identified were emodin, emodin monomethyl ether, chrysophanol, fat, resin, the sugars, xylose and rhamnose, rhamnol, an alcohol of the quebrachol type and which was identified with the phytosterol obtained from *Cascara* and *Rumex* species. L. E. WARREN

Synthetic drugs. SOC. ANON. POUR L'IND. CHIM. A BÂLE. Brit. 185,913, July 20, 1921. 2-Phenyl-4-quinolinecarboxylic acid, or a deriv. or substitution product, is converted into a 2-phenyl-4-quinolyl alkyl ketone by condensing its ester with a fatty acid ester in presence of EtONa and subjecting the 2-phenylquinolyl ester so obtained to the ketone hydrolysis; or the nitrile of 2-phenyl-4-quinolinecarboxylic acid may be converted into the alkyl ketone by the Grignard reaction. The amino alcohol is obtained from the ketone either (a) by reduction of its isonitroso compd., or (b) by halogenizing the alkyl group, condensing the halogen compd. with an amine, such as dimethylamine, and reducing the amino ketone so obtained. The products are more active towards paramacia than the corresponding non-phenylated compds.

18*-ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

A new hattery of tourilles for the manufacture of hydrochloric acid. H. J. PAOLI. *Anales asoc. quim. Argentina* 10, 99-111(1922).—Illustrations of working installations of many types of tourilles are given. An objection to most of the forms in use is their fragility due to their odd shapes. Many are difficult to cool. The new form described consists of a cylindrical jar set in a tub of water for cooling. The liquid acid circulating through the series enters at one side near the top, is deflected to the bottom by a tube inside the jar and leaves at the opposite side near the top in a manner similar to the Putzer form. The jar has a removable dome-shaped cover with large gas inlet and outlet separated by a partition across the inside of the cover which deflects the gas stream downward to promote absorption by the liquid. L. E. G.

Post-war progress in the fixation of nitrogen. J. A. HARKER. *J. Soc. Chem. Ind.* 41, 387-90R(1922).—A review. W. H. ROSS

Sodium silicate as an adhesive. REX FURNESS. *J. Soc. Chem. Ind.* 41, 381-4R(1922).—Sodium silicate is a cheap, fireproof, water-resistant, odorless adhesive which is easy to apply and does not putrefy and decay. It sets by cooling or by loss of water. Its properties may be controlled by changes in concn. or in compn. In con. solns. the latter may be anything from $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ to $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$. The viscosity varies inversely with the alkali content [not strictly true—ABSTR.] or directly with the gravity and may be regulated to give the desired penetration. Na silicate adhesives are used in corrugated and solid fiber boards, wall board, veneers, and abrasive wheels. Staining due to the alkali may be avoided. Fillers change the viscosity and setting time but the resulting mixts. are harder to use. WM. STERICKER

Industrial methods of liquefaction and practical applications of low temperatures (MURRAY) 13.

Hydrofluoric acid. H. HOWARD. Brit. 186,606, Sept. 18, 1922. HF is prepd. free from Si compds. by passing the gases evolved on treating fluorspar, containing SiO_2 , with H_2SO_4 into a soln. of K_2SO_4 . The SiF_4 and H_2SiF_6 form K_2SiF_6 , which collects as a ppt. and the HF is not appreciably condensed, as the scrubbing soln. is kept hot. The ppt. is removed periodically and the acid liquor contg. H_2SO_4 which accumulates is utilized in the decompn. of more fluorspar. K_2SO_4 may be recovered from the ppt. of K_2SiF_6 by decomposing with H_2SO_4 , distg. off the H_2SiF_6 evapg. and leaching the residue in order to sep. the SiO_2 which is also present from the K_2SO_4 .

Recovering nitrona vapors. P. A. GUYE. U. S. 1,433,004, Oct. 24. Nitrous vapors such as contain an excess of N and O are brought into contact with glass wool, cotton or other acid-resisting fibrous material impregnated with H_2O , to form HNO_3 soln.

Alkali compounds from silicates. PLAUSON'S (PARENT CO.), LTD. Brit. 186,199, July 15, 1921. Alkali compds. are extd. from minerals contg. alkali in an insol. or difficultly sol. form by subjecting the mineral to intensive mech. disintegration at a peripheral speed of at least 1000 m. per min., preferably in the colloid mill described in 155,836 (C. A. 15, 1788), before or during chem. or electrochem. treatment. The extn. is preferably carried out after pre-treatment, such as by heating with carbonaceous material or with reducing gases. The ground mineral may be allowed to stand in a dil. mineral acid and then treated in the colloid mill, either with or without superheated steam and high pressure; or it may be treated directly or with superheated steam; or it may be first peptized with H_2O , and then treated with acid or alkali. The mineral dispersion may also be electrolyzed. In an example ground felspar is allowed to stand in dil. HCl, the mixt. dild. and peptized and the dispersion heated in an autoclave to about 225° at a pressure of 25 atms. The soln. is filtered and concd.

Potassium chloride from brine. J. L. SALSBERG. U. S. 1,432,796, Oct. 24. Salts from evapg. of natural brine, containing chlorides of Mg and K, are washed with KCl liquor at atm. temp. to dissolve out MgCl_2 and to force some KCl out of soln. by replacement with MgCl_2 . A bot. satd. soln. is then formed from the solid residue and on cooling this soln. KCl is deposited.

Potassium nitrate from greensand and sodium nitrate. T. C. MEADOWS, M. HAUBER, JR. and H. W. CHARLTON. U. S. 1,433,290, Oct. 24. Greensand is digested at a temp. of about 245° under steam pressure for 40 min. with CaC, NaOH and NaNO_3 to form KNO_3 . NaBr, NaNO_2 , Na_2SO_4 , NaClO_4 or other Na salts may also be used to effect production of the corresponding K salt instead of KNO_3 .

Drying chlorine. G. A. RICHTER. U. S. 1,431,981, Oct. 17. Wet Cl is brought into contact with a refrigerated soln. such as a 30% CaCl_2 soln. chilled to about -10° , in a filled scrubbing tower.

Cyanamide. WARGONS AKTIEBOLAG and J. H. LIDHOLM. Brit. 186,020, May 17, 1921. In the production of solns. of free cyanamide by gradually adding CaCN_2 to a circulating body of H_2O or cyanamide soln. into which CO_2 is admitted, the process is carried out in such a way that the quantity of liquid between the points where the CaCN_2 and CO_2 , resp., are supplied is const. and small compared with the total quantity of liquid, notwithstanding the increase in bulk owing to the addn. of CaCN_2 . The result is that each addn. of CaCN_2 is only in the liquid a short time before reaching the CO_2 and only a small proportion of the liquid is alk. A suitable construction is specified.

Nickel. H. E. FIERZ and H. A. PRAGER. Brit. 186,457, July 14, 1921. In a method of obtaining Ni from $\text{Ni}(\text{CO})_4$ in which the gases contg. the $\text{Ni}(\text{CO})_4$ are passed over heated surfaces, means are provided for cooling the gases in the body of the app. A suitable app. is specified.

Nickel. H. E. FIERZ and H. A. PRAGER. Brit. 186,458, July 14, 1921. Ni is deposited from $\text{Ni}(\text{CO})_4$ by passing the gases contg. the $\text{Ni}(\text{CO})_4$ between a no. of parallel heated surfaces arranged close together, say from $1/2$ to 1 in. apart. A suitable app. is specified.

Coating compositions. BRITISH THOMSON-HOUSTON CO., LTD. Brit. 185,910, July 18, 1921. A coating compn. particularly adapted for *frosting glass* is obtained by peptizing kaolin or other body material by the addn. of a NaOH or other soln. contg. hydroxyl ions, and adding thereto an inorg. binding agent, such as Na_2SiO_3 . Opacifying and coloring ingredients, e. g., the oxides of Mg, Al, Zr, Sn, and Zn, may be added to the compn., and a small addn. of AmOH may be made to reduce its surface tension. The coating may be hardened after application by means of a fixing soln. consisting of ZnCl_2 and $\text{Al}_2(\text{SO}_4)_3$, or of other sol. salts of Zn, Sn, Mg, Ca, etc., which react with the binding agent.

Coating compositions. J. DAVIES and W. H. MILES. Brit. 186,231, Aug. 24, 1921. A prepn. to be applied to metallic surfaces before magnesium oxychloride cements are applied thereto consists of CaF_2 , CaCO_3 , and a soln. of Na or K silicate with or without powd. clay, such as pipe-clay or china clay. Suitable proportions are CaCO_3 , CaF_2 , and clay 10 lb. each, and Na_2SiO_3 soln. of 33° B $\acute{\text{e}}$. 18 lb. According to the Provisional Specification the clay is replaced by calcined magnesite.

Preventing condensation on glass. E. BOUCHAUD-PRACEIQ. Brit. 186,615, Sept. 26, 1922. The collection of condensed moisture on glass, particularly on wind screens, is prevented by wiping the surface with soft paper in which is incorporated an alk. soap together with oil-absorbing substances such as alk. earth carbonates or borates or kieselguhr.

Plastic compositions. IMPERIAL TRUST FOR THE ENCOURAGEMENT OF SCIENTIFIC & INDUSTRIAL RESEARCH AND S. B. SCHRYVER. Brit. 186,157, June 21, 1921. Proteins obtained from the residues of oleaginous seeds from which the oil has been expressed, or the residues themselves, are used in conjunction with an alkali as binding agents in plastic compns. Suitable raw materials are the residues of castor beans, cottonseed, hempseed, and linseed. The alkali may be replaced by a mixt. of an alkali carbonate and an alk. earth, with or without an alkali salt, such as NaF, which reacts slowly with the alk. earth. Fillers, such as powd. slate, asbestos, sawdust, or sand, may be included in the compn., or the seed residues themselves may act as fillers. Pigments may also be added. The ingredients are ground up together with H_2O , and molded either with or without pressure. Numerous examples of proportions are given. Cf. 140,911. (C. A. 14, 2245.)

Plastic compositions. L. LEW. HAMON. Brit. 186,355, Sept. 13, 1921. Four compns. contg. peat are described for the manuf. of bricks, building blocks, etc.: (1) 70 parts by vol. of peat, 25 of CaO , 5 of ZnSO_4 ; (2) 75 parts of peat, 20 of CaO , 1 of alum, 2 of tar, 2 of gypsum or silicate of soda; (3) 45-50 parts of peat, 45 of clay, 5-10 of silicate of soda; (4) 30-35 parts of peat, 60 of clay, 5-10 of silicate of soda. The peat as it comes from the bog is macerated, the other ingredients are added, and articles are molded. In the case of compns. (1) and (2), articles harden without artificial heat; other articles are burned. Reinforcements may be inserted during molding.

Molding casein. COMPAGNIE GÉNÉRALE D'ÉLECTRICITÉ. Brit. 186,352, Sept. 25, 1922. Casein or materials having a casein base are molded into homogeneous polished plates by laminating the agglomerated material by rolling it into sheets, which are then pressed into block form in a mold having a polished surface or lining. Marbled effects may be obtained by mixing in differently colored particles during the lamination. The mold may be smeared with grease or soap to prevent sticking.

Friction facings. L. KIRSCHBRAUN. Brit. 185,809, June 1, 1921. Friction

facings for clutches, etc., are made by satg. a mixt. of incombustible fibrous pulp and comminuted phenol resin with a hinder and baking. The hinder may be a soln. of bitumin of low m. p. in gasoline, benzene, toluene, or gas oil. The finished product has a tensile strength exceeding 2000 lb. per sq. in. and Brinnell hardness exceeding 10.

Heating-cartridges. HIRSCH, KUPFER- UND MESSINGWERKE AKT.-GES. Brit. 186,617, Sept. 27, 1922. A cartridge contg. a thermoaluminic or like mixt. has its casing or envelope formed of Al or other easily combustible metal or alloy capable of partaking in the chemical reaction.

Powdered carbonaceous char. H. RODMAN. U. S. 1,433,039, Oct. 24. A mass of powdered coking coal is gradually heated to a coking temp. by applying a slow external heat to the receptacle within which the material is placed and the powd. form of the material is maintained during coking by agitation. The product thus obtained may be used for absorbent purposes or as a pigment in paints.

Dental investment composition. L. J. GILBERT. U. S. 1,432,545, Oct. 17. Plaster of Paris I, is mixed with SiO_2 2 and Portland cement 3 parts.

Lithographic plate treatment. D. P. BARNETTE, JR. U. S. 1,433,111, Oct. 24. After a subject on a lithographic plate has been "washed out" a hardened film is formed on it by application of a soln. of ink- and etching-soln.-resisting material, e. g., a soln. of shellac in alc., AmOAc, essential oils and "violet crystals."

Impregnating clay with carbon. W. SMITH. U. S. 1,432,629, Oct. 17. Articles of clay satd. with C and adapted for resisting acids and high temps. are prepd. by mixing clay with coke or oil shale and heating the mixt. out of contact with air to expel H_2O and volatilizable matter and leave a C residue within the clay.

Acid-proof tank linings. R. T. WALES. U. S. 1,433,315, Oct. 24. Tank linings are formed of acid-resisting cement molded in section *in situ* and after the sections constituting the main portion of the lining have shrunk the spaces between them are filled with narrow pieces of similar molded material.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Detecting stoppages in furnaces by vacuum readings. HENRY W. HESS. *Glass Worker* 42, No. 4, 13(1922).—Under normal conditions a glass furnace should show a positive pressure of the contained gases at the edge of the crown. Half way down, the gases should show a slight pressure and at the floor level, the condition should be approx. balanced between pressure and vacuum. At the outlet of the waste gas checkers there should exist a slight vacuum, while a waste gas flue which does not leak too much should show a steady rise in vacuum to the base of the stack where it should incurve from $\frac{1}{8}$ " to $\frac{1}{4}$ ". J. B. PATCH

Coating compositions [for glass] (Brit. pat. 185,910) 18.

Recuperator for glass furnaces. W. McLAUGHLIN. U. S. 1,432,706, Oct. 17. Structural features.

Waterproofing tile and similar articles. J. T. POKORNY. U. S. 1,433,120, Oct. 17. After burning tile or the like in a furnace, coal tar is poured into the hot furnace and the latter is closed to exclude moisture and permit tar vapors to be absorbed by the tile.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Spontaneous combustion of coal. T. DRESCHER. *Chem.-Zig.* **46**, 802-3(1922); cf. Binder, *C. A.* **16**, 4045.—A black pigment used by the paint industry and sold under various trade names is essentially coke (lignite coke, bone charcoal, etc.). It is prepared by grinding, sometimes extending over a period of 24 hr., in edge-runner mills or closed drums, and is discharged warm. However, no case of spontaneous combustion is known. Attempt was made to substitute therefor a good quality of coal containing pyrites. This ground material took fire in storage and was removed out of doors on to frozen ground. On removing the top bags after about 2 weeks, the contents of the lower ones were found to have been burned. The material was repacked in new bags and in a few days took fire again. The spontaneous combustion is held to be due to the oxidation of the pyrites by air and moisture. Sufficient air will always be present between the particles to start the action. J. L. WILEY

Possibility of spontaneous combustion being initiated by the heat produced in crushing. HENRY BRIGGS. *Iron Coal Trades Rev.* **105**, 715-6(1922).—The production of heat by the act of crushing or grinding coal or carbonaceous shale is one of the causes leading to spontaneous combustion in mines; the rise in temp. induced is inversely as the diam. of the particle produced since fine particles gain a higher initial temp. and offer a greater surface for oxidation. A fragment of av. bituminous coal 1/300 in. diam., if suddenly produced by crushing, will, in the midst of similarly conditioned particles, obtain a temp. rise of about 52° F. while the temp. rise of a particle 1/100 in. diam. will equal be about 17° F. The heat developed in crushing bituminous coal is found to be to 0.00036 B. t. u. per sq. in. of fractured surface, while that in crushing Birchenwood shale is 0.00077 B. t. u. per sq. in. The heat generated by crushing is distributed very rapidly through the particle; in 1/500 sec. after crushing, the temp. of the surface of a coal fragment 1.25 in. in diam. is only 3% above the general temp. of the fragment. In the majority of cases, the direct thermal action of crushing is probably confined thus to warming up the fractured particle sufficiently to start accelerative oxidation which may be followed by active combustion. J. L. WILEY

Some aspects of cleaning coal by froth flotation. L. A. WOOD. *Iron Coal Trades Rev.* **105**, 732-3(1922).—Froth flotation is limited in general and at the present stage of development to coal particles of a size $1/10$ in. or less, and is therefore an ideal process to work in conjunction with a jig-washer which can handle efficiently only sizes above that. The process is commercially and technically efficient, the cost of operation for a 25-40 ton per day plant being about 4.5 d. per ton of material treated. The difficulty is to dry the flotation concentrates to a suitable degree of moisture. Initially they contain 50% of water. Ordinary drainage will reduce this to 18 or 20%; drainage in tanks with filter bottom to 16-18%; and suction filters of the Oliver type to 11-14%. Drying by heat is not advisable. A simple practical method which reduces the moisture content to from 9.6 to 5.3% consists in mixing with the flotation product 4% of tar and pressing at a pressure of from 1 to 4 tons per sq. in. in an ovoid briquet press. The soft briquets lose water very rapidly on standing, the moisture content of one pile falling from 9.7 to 2.5% in 24 hr. It is thought that for dry charging to coke ovens the briquets will not require crushing but that natural breakage in handling will be sufficient to fill the voids. A plant of 3-5 tons per hr. capacity is nearly ready for operation. J. L. WILEY

Problem of bituminous coal washing and measures now being taken for their solution. G. R. DELAMATER. *Coal Age* **22**, 664-6(1922).—This is the first part of an

article dealing with coal washing problems and is largely a review of the different methods of wet and of dry washing and the relative advantages and disadvantages of each method. Emphasis is placed on the value of screening out the fines or carefully sizing the coal before the washing process is begun.

W. W. HODGE

Notes on a Manchurian coal from Fushun. G. W. HIMUS. *J. Soc. Chem. Ind.* **41**, 333-4T(1922).—The location, geological description and coal reserves of the Fushun Colliery are given. Analyses of Fushun coal given show that it averages over 40% volatile matter, low ash, about 12500 B. t. u. It is a poor coking coal. It contained approx. 3.3% of little altered resin-like substances. The CHCl_3 ext. of this material analyzed as follows: volatile matter 97.3%; fixed C 1.1%; ash 1.6%; B. t. u. 16550; C 79.22%; H 9.80%; O 10.19%; no S or N. Comparative analyses are given of the coal, the resinous matter, and the non-resinous lumps, respectively, as follows: volatile matter 41.7, 51.5, 46.0%; fixed C 48.5, 28.8, 49.2%; ash 9.8, 19.7, 4.8%; S 0.5, 0.15, 0.75%; B. t. u. 12410, 12530, 13920. The sapon. no. of the resinous material was 130; the m. p. was 140°. The resinous matter tends to be concd. with mineral matter in bands throughout the coal. The non-resinous lumps of coal contain about $\frac{1}{4}$ as much CHCl_3 extractable material as the resinous; they are freer from mineral matter and have a strong action on a photographic plate.

W. W. HODGE

Disintegration of coal by acids. R. LESSING. *Iron Coal Trades Rev.* **105**, 724-5, 776(1922).—When coal is treated with acids, there results a decompn. of the interstratified carbonates, serving as the cementing medium between the coal particles, and a sepn. of the coal substance proper along the cleats or partings. The kind of acid to be used is immaterial, but gaseous acids, such as SO_2 or CO_2 , by their greater penetrating effects, are more efficient in massive coal. An interesting application is to the mining of coal whereby SO_2 gas, applied to the coal seam by means of borings, is rapidly absorbed by the coal, and causes a disintegration of the coal bed, thus avoiding the use of explosives or mech. methods. An impure quality of SO_2 , easily produced from coal pyrites or from H_2S extd. from coke oven gas, would be entirely suitable. The amt. needed should not exceed 1 ton of SO_2 per 1000 tons of coal, at a cost of about 2.5 d. per ton of coal. The use of this gas in mines is not considered dangerous to workmen as it is readily absorbed by the coal and thus removed from the air. Furthermore, its use may form a safety factor, since unfinished expts. indicate that the ignition temp. of coal is raised by treatment with SO_2 . Another application is in coal cleaning. By treatment with acid the sepn. of fusain, durain, clarain, and vitrain from each other and from the inert substances, such as ankerites, shale and pyrites, is facilitated.

J. L. WILEY

Colloidal oil for laying coal dust. G. K. S. MONCRIEFF. *Iron Coal Trades Rev.* **105**, 730-1(1922).—A colloidal emulsion of oil has been found to be capable of satg. coal dust in mines and keeping it in a moist condition for sometime without further treatment. It is not objectionable to handle nor dangerous to the health. Traffic only serves to improve the condition of the dust. It has no adverse effect on the natural strata but leaves an oily film which appears to have a beneficial effect. Lab. tests show that it does not increase the liability to explosion of the dust, but further tests in this connection are necessary. At present the cost can hardly be compared with that of stone dust.

J. L. WILEY

Burning anthracite duff under boilers. ANON. *Iron Coal Trades Rev.* **105**, 733 (1922).—Anthracite duff has previously been found useless as fuel notwithstanding its high calorific value. A typical anal.: av. B. t. u. 13137, volatile matter 4.59%, ash 9.44, fixed C 83.6, hygroscopic moisture 2.37. However, recently, tests carried out with a Turbine Furnace with specially constructed grates for better distribution of the air to the fire bed and with steam pressures on the jets of from 40 to 85 lb., giving an air pressure under the grates of 0.45 to 1 in., resulted in evapns. of 4250 to 4875 lbs. of steam per hr. The new grates are described and illustrated.

J. L. W.

Our (French) resources in liquid fuels. P. MALLET. *J. usines gas* **46**, 305-8 (1922).—Cf. Mailhe, *C. A.* **16**, 4046. J. L. W.

A process for the production of industrial absolute alcohol and its application to the preparation of a domestic motor fuel. C. MARILLER AND VAN RUYMBEKE. *Compt. rend.* **175**, 588-90 (1922).—A process is developed for making com. abs. EtOH at only a slightly higher cost than com. 95-6% EtOH by means of liquid instead of solid dehydrating agents. Of all liquids glycerol was found most efficient. EtOH contg. H₂O is distd. in a rectifying column down which is passed a current of glycerol. From 95% EtOH, 98.5-99% EtOH can be obtained directly, and the process can be used to concentrate dil. vapors as well. Glycerol is recovered by distg. off the EtOH at atm. pressure and the H₂O *in vacuo*. To obtain EtOH over 99% glycerol contg. CaCl₂, K₂CO₃, KOAc or ZnCl₂ is used. These solns. are made by dissolving the salt in H₂O, adding to glycerol and evapg. the H₂O *in vacuo*. K₂CO₃ is recommended as the most efficient, a 30% soln. giving 99.9% EtOH. C. C. DAVIS

Methane. Properties, constants and uses. J. BRONN. *Chem.-Ztg.* **46**, 926-7 (1922).—CH₄ is now available commonly in Germany in cylinders at 150 atm. The gas is 90-92% CH₄, the rest C₂H₆, H₂, and N₂, and is free from dust and condensable vapors. When used in place of H₂ the same orifices may be used, and about 1/2 more air must be admitted. CII₄ may be used as a substitute for, or supplement to, city gas. It is especially advantageous for the cutting and welding of Al and brass, giving a "soft" flame with plenty of heat, and a strongly reducing atm. when required. Since CH₄-air mixts. may be highly compressed without ignition, they can be used with high efficiency in motors, either exclusively or for starting. Some directions for use and tables of properties are given. ERNEST W. THIELE

Compressed methane. J. BRONN. *Z. angew. Chem.* **35**, 612-4 (1922).—The low combustion rate and the narrow combustion limits make the methane Bunsen flame tend to leave the burner. This can be avoided by protecting the base of the flame with a metal cylinder slipped on the burner. To overcome the Joule-Thomson cooling it is best to halve the cylinder pressure by filling an empty cylinder from a full one. Several pressure governors for high pressure are described. Cf. preceding abstract. ERNEST W. THIELE

Murray's improved complete gasification plant. E. F. MURRAY. *Gas J.* **160**, 435-6 (1922).—The plant is of the type in which a retort is placed above a water-gas generator, operated on the usual blow and run system. The gases produced during the blow are burned in checker chambers around the retort, and those produced during the run are passed through the fuel in the retort. A space is left at the top of the retort for the purpose of drying the fuel and distg. off the lighter volatile constituents by means of the sensible heat of the run gas. Such volatile portions are passed into carburetting chambers, situated adjacent to and heated by the generator charge, and are cracked into permanent gases. Additional carburetting material may be introduced into the vaporizing space at the top of the retort. The gases thus fixed pass up through the retort together with the run gases and into an annular space around the retort heated by the blow gases. In this way all the hydrocarbon vapors of the run gas are converted into permanent gases. J. L. WILEY

Problems of condensation [of coal gas]. GEO. LAURIE. *Gas J.* **160**, 502-3 (1922).—Comparison is made between the atmospheric and the water-cooled types of condensers. The only advantage of the former is its extremely low maintenance cost. The advantages of the latter are: the low initial cost, about 1/2 that of the atm. type; the comparatively small space occupied; and its adaptability to weather conditions and easy regulation to a wide variation in make of gas. Its disadvantage is the cost of providing an adequate water supply. The surface capacity per 1000 cu. ft. of gas is 6 to 10 sq. ft. for the for-

mer and 3 sq. ft. for the latter type with a consumption of up to 3 gal. of water per 1000 cu. ft. per day.

J. L. WILEY

Liquid purification at Battle Creek, Mich. F. W. SEYMOUR. *Gas Age-Record* 50, 765-7(1922).—An installation of the Scaboard process (*C. A.* 16, 2594) has been in operation since June 15, 1922. The cost of purification represents a saving of nearly 1 cent per M over 1920 and 1921. Water gas is being purified along with coal gas without affecting the activity of the solution. To date all indications point to a complete cure of meter deterioration due to cyanogen. The only disadvantage experienced is the question of odor in the foul actifying air emanating from the vent pipe.

J. L. W.

Industrial uses of gas. Realization of an ideal burner. ANON. *J. usines gaz* 46, 327-35(1922).—Application to surface combustion.

J. L. W.

New mechanical grates and ash removers for producers, especially for those with elongated shafts. Gwosdz. *Feuerungstechnik* 10, 269 73(1922).—G. describes and illustrates 12 automatic continuous devices for removing ashes from producers of rectangular cross section.

ERNEST W. THIELE

Low-temperature carbonization and the therm. WALTER CHANEY. *Gas J.* 160, 387-8(1922); cf. *C. A.* 16, 4320.—A continuation of statistical investigations of works mfg. results in order to show that the use of low-temp. gas as an curicher instead of oil is profitable.

J. L. WILEY

Low-temperature carbonization and the economics of manufacture. GEO. FVETTS. *Gas. J.* 160, 427-8(1922).—E. points out some fallacies in Chaney's calens. (see above abstr.).

J. L. W.

Determination of benzene in gas. H. BÄHR. *Chem.-Ztg.* 46, 804(1922); *Gas u. Wasserfach* 65, 608-9; cf. Krieger, *C. A.* 16, 2771.—A jacketed metal cylinder filled with activated charcoal and placed in a vertical position is used for the absorption. After absorption is complete the cylinder is placed in a horizontal position and the jacket partly filled with solvent naphtha (b. p. 160-170°). The naphtha is heated to boiling and a stream of superheated steam passed through the charcoal. The benzene is thus condensed and the app. is swept out with heated gas. After cooling the app. is ready for a second detn. Tests with this app. at a coke-oven plant showed that absorption losses were over 25%. Part of this loss is unavoidable however, the charcoal app. recording as benzene fractions of very low b. p. which are not retained by the wash-oil.

J. L. WILEY

Determination of hydrocarbons in industrial gases. WOLLERS. *Z. angew. Chem.* 35, 536(1922).—The method involves fractional sepn by means of low temps. The app. consists of a spherical condensation flask and a Hg-air pump. 100 cc. of the gas are admitted to a buret under atm. pressure. The air is exhausted from the app. and the flask cooled with liquid air after which the gas is admitted and cooled for about 10 min. and these p. fractions are pumped off. Fraction I from -180 to -190° contains O₂, H₂, CO, CH₄ and N₂; these are detd. by combustion. Fraction II from -115° contains C₂H₄, C₂H₆, and part of the C₃H₄ and C₃H₆. C₂H₂ can be removed by absorption in a K-Hg-I soln. The C₂H₄ hydrocarbons can be quantitatively absorbed in concd. H₂SO₄ to which some V₂O₅ is added, or they can be passed over Pd-black with an excess of H₂ and converted into the corresponding paraffin hydrocarbons which can be sepd. by fractional distn. Fraction III from room temp. contains the rest of the C₃H₄ and C₃H₆, C₄H₈ and C₄H₁₀. This fraction is burned in the Drehschmidt app. For detg. only the satd. hydrocarbons fraction I is obtained as above and fraction II at room temp. The CO₂, C₂H₂ and the C₃H₄ hydrocarbons are absorbed. After the absorption the gas is passed again through the fractionating app. and split up into fractions II

and III as above. The fractions are likewise burned. Several check tests have shown that this is an excellent method for sepn. of gaseous paraffin hydrocarbons.

J. L. WILEY

Explosions in flues and stacks. HENRY W. HESS. *Glass Worker* 42, No. 3, 13 (1922).—It is possible to explode under normal pressure a mixt. of 6% of city gas dild. with 94% of air, and the reverse percentages may likewise be exploded. Max. detonation is reached with about 1 part of gas to 6 parts of air. A temp. of 1150°F. detonates ordinary city or coke oven gas. Similar explosions but of less violence occur with the use of producer gas. Leakages of air and gas into stack flues should be avoided.

J. B. PATCH

Tar distillation. W. A. WALMSLEY. *J. Soc. Chem. Ind.* 41, 296-8T(1922).—Vertical retort tar considered as being a mixt. of high and low temperature tar was compared with horizontal retort tar and found to contain less benzene, little $C_{10}H_8$, a large percentage of material sol. in NaOH but which contained little phenol. The vertical retort tar contained less pitch and more total oils. Distn. data are given. R. L. B.

Determination of phenols in mixtures of tar acids. W. H. HOFFERT. *J. Soc. Chem. Ind.* 41, 334-7T(1922).—Equal wts. of the 3 cresols produce equal lowering of the temp. at which phenol hydrate seps. from mixts. of the acids with water. For the detn. the tar acids are freed from all but 2-3% of neutral hydrocarbons and pyridine bases. Xylenols or higher homologs are removed by fractionation with a good column. The mixt. is then brought to above 55% PhOH by adding a known wt. of pure PhOH. Ten % of its wt. of water is added to the mixt., and the f. p. detd. by noting to 0.1° the temp. at which the cloud of fine crystals (produced by supercooling and seeding) disappears. The % PhOH in the anhydrous mixt. and the f. p. of the mixt. when 10% water is added are: 100%, 16.0°; 95, 14.25; 90, 12.25; 85, 10.25; 80, 8.1; 75, 5.8; 70, 3.4; 65, 0.75; 60, -2.2; 55, -5.2. The method can be used for crude carboic acid when the latter is freed from water and higher homologs by fractionation and salting out. It is rapid and not greatly influenced by small traces of moisture in the sample.

ERNEST W. THIEL

Decomposition processes applicable to certain products of coal carbonization. M. J. BRADLEY AND S. W. PARR. *Chem. Met. Eng.* 27, 737-44(1922).—A paper impossible to abstract in its entirety, but summarized as follows: (1) Mixed xylenes were decomposed by heat and contact surfaces, under the stabilizing influence of H and methane. Sixty-nine % of the original xylene was converted into crude benzene, which boiled below 100°. This is approx. 94% of the theoretical. (2) At slightly lower temps., under the same condition of contact surfaces but in a gaseous atm. largely ethylene, 77% of the mixed xylenes were converted into higher boiling substances principally solids. (3) Mixed xylenes under other conditions were converted into toluene, yield 64%. (4) Mixed xylenes decompd. by heat in contact with iron surfaces yielded quantitatively amorphous C and gas. Slightly reduced iron oxide accelerated the reaction. (5) Non-metallic substances like charcoal, pumice or refractory material at like temps. tend to decompose xylenes into unsatd. and higher boiling compds. (6) Activation of heated Fe and C surfaces could be induced by a short treatment with superheated steam and then slightly reduced with hydrogen. (7) Air, superheated steam, CO_2 and CO passed through the activated furnace poisoned the catalyst. The liquid hydrocarbons were most stable under these conditions. (8) Contact surfaces are very important to hydrogenation and dehydrogenation of aromatic hydrocarbons. (9) Gases like methane and N_2 between 600 and 700° have mostly a mech. action on pyrogenic decompn. C_3H_4 , C_2H_2 , H_2 , and ethane also act similarly but their all-important action is chemical. With the exception of H_2 they were decompd. above 725°. (10) C_2H_4 under proper conditions gave pure CH_4 or CH_4 plus C_2H_6 . R. L. B.

Ignition temperatures of coke. K. BUNTE AND A. KÖLMEL. *Gas u. Wasserfach* 65, 592-4(1922).—The app. used for the detn. consisted of a vertical elec. oven, in which the coke was slowly heated in a regular stream of air preheated to the prevailing oven temp. For this purpose, the lower part of the tube was filled with broken fireclay, above which the coke was placed and sepd. off by wire gauze. A thermocouple, protected by a quartz tube, was suspended in the coke to within 2 or 3 mm. of the bottom of the column. This showed the rise in temp. in the oven, and it was found that at the moment when the ignition of the coke begins, a very marked jump in temp. takes place. Air was passed at the rate of 15 l. per hr. The ignition temps. detd. for coke 3 to 5 mm. in size were for semi-coke 395°, for gas coke 505°, for coke-oven coke 640°, and coke from continuous ovens 530°. The ignition temps. gradually decreased with an increase in the rate of air flow. Size of coke also plays a part in this respect. Gas coke and coke-oven coke of 0.5 to 1 mm. had an ignition temp., resp., of 477 and 590°, 1 to 3 mm. 492 and 612°. There was found no traceable relation between ignition temp. and vol. of porosity. The fact that ignition temp. was found to depend, to a large extent, upon O concn. and upon the size of coke goes to show that those characteristics are of most influence which are connected with the degree of fineness of division of the coke substance. An apparent connection between volatile constituents and ignition temp. could not be traced to any detg. characteristic. It is believed that the method of carbonization, and mainly, perhaps, the speed, is an important factor. Further research is in progress.

J. L. WILEY

The lignin origin of coal, a geologic and paleontologic impossibility (POTONIK) 8.
The origin of bituminous coal and anthracite (ROBERTS) 8.

Mixture of liquid and solid fuels. C. J. GREENSTREET. U. S. 1,432,178, Oct. 17. Powdered coal or similar solid fuel in finely divided form is mixed with a liquid fuel such as tar or petroleum oil and the latter is then oxidized by the action of air (or otherwise treated) in order to increase its viscosity and maintain the solid particles in suspension. Cf. C. A. 16, 3384.

Motor fuel. H. KLEINSCHMIDT. Brit. 185,796, May 11, 1921. Naphthenic acid is added to hydrocarbons in amts. of at least 5% and up to 40% by vol. to form a motor fuel; or the acid is used in the form of its neutral or acid soaps to form fuels of the type described in 12,325, 1914, in which H₂O is incorporated as an emulsion. Phenols, preferably in proportions of 1-3% by vol., or amyl or ethyl alc. may also be added.

Motor fuel. T. M. HICKMAN. Brit. 186,106, June 9, 1921. Fuel oil for internal combustion engines comprises an intimate mixt. of mineral hydrocarbon oils (d. 0.865-0.895), resin oil or oil derived from heating resin or a resinous body, and H₂O with or without distd. or recovered grease, fatty oils, tar distillates, or cracked or polymerized mineral oil, the constituents being incorporated by NH₃ or NMe₃. The resinous and fatty constituents may be nitrated or sulfonated. The tar distillates used contain tar acids and boil between 250-280°.

Flotation of coals. F. G. PRICE AND MINERALS SEPARATION, LTD. Brit. 186,143, June 20, 1921. The flotation of fusain, and other undesirable constituents is prevented by the addition of a small proportion of a protective colloid, with or without the assistance of a frothing agent such as cresol or paraffin, previous to the aeration and agitation of the pulp. The protective colloid may be tannin, starch with or without NaOH, dextrin, tapioca, maize flour, egg albumin or blood albumin, neutral or alk. casein, animal gluten, gelatin, glues, cutch, or agar-agar.

Apparatus for distilling volatile hydrocarbons from coal, shale or lignite. C. C.

BUSSEY. U. S. 1,432,275, Oct. 17. The app. comprizes a columnar frusto-conical retort with a grate at its base for supporting a mass of coal, shale or lignite above an ignited fuel bed. Mechanism is provided for removing solid residue from the base of the retort and hydrocarbon vapors are withdrawn from the top of the retort and led to a condenser. Fresh material for distn. is fed to the top of the retort simultaneously with removal of residue from the bottom. U. S. 1,432,276 relates also to use of an ap. of this construction.

Retorts. LOW TEMPERATURE CARBONIZATION, LTD., LOW TEMPERATURE CONSTRUCTION, LTD., AND T. M. DAVISON. Brit. 185,778, March 21, 1921. A retort for the distn. of coal, etc., is provided with collapsing plates mounted centrally within and extending across the retort in such a manner as to be brought into close proximity be means of relative longitudinal movement.

Gas manufacture. R. F. MURRAY. Brit. 185,887, July 1, 1921. In a complete gasification plant in which a retort is superposed on a water-gas generator and externally heated by the combustion of the "blow" gases, the fresh fuel is heated in an upper extension of the retort and the vapors from the tar-forming constituents are passed into a carburetting chamber heated by the generator and thence into the water gas during the "run."

Testing calorific value of gas. C. H. LANPHER. U. S. 1,432,472, Oct. 17. Gases of known and unknown calorific value are successively burned in a Bunsen burner and the difference in the adjustment of the burner necessary to render the flame non-luminous is noted on graduations on the burner.

Sulfur recovery from gas. K. COX, R. P. KERR and R. J. BAY. Brit. 185,780, April 7, 1921. The gas is passed through a contact material such as Fe_2O_3 or Al_2O_3 . The temp. of the reaction is so controlled that deposition of S on the material is prevented and the S is carried by the effluent gases and collected by deposition in the elemental state. A suitable app. is specified. Cf. 3608, 1882, 5959, 1883, 13,844, 1896, 20,920, 1908 and 120,554.

Sulfur recovery from gas. GBS. FÜR KOHLENTCHNIK. Brit. 186,316, Aug. 14, 1922. H_2S is removed from gases by washing with a Ni salt soln. with or without the addition of a salt incapable of pptg. Ni, or of a substance capable of forming a Ni compd. sol. in alk. solns., e. g., NH_3 , pyridine, salts of organic acids, NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ and NaCl . When the H_2S has been absorbed, with the formation of a ppt. of NiS , air is blown in to produce free S and of a Ni soln. suitable for re-use.

Feeding device for gas producers. O. T. BROWN. U. S. 1,433,109, Oct. 24.

Distilling tars. F. DUPLAN. Brit. 186,616, Sept. 27, 1922. Tar is distd. in the presence of a powdered or granular solid, such as CaCO_3 , sand, coke, charcoal, etc., or a substance which has a chem., phys. or catalytic action upon the tar. Frothing is prevented and shallow retorts may be used. From vegetable tar are obtained products which may be used as fuel in Diesel engines or mixed with alc., benzene, petroleum, etc., as fuel for motor-car engines.

Coking process. S. R. ILLINGWORTH. Brit. 183,384, May 26, 1921. Addition to 164,104 (C. A. 16, 1312). Coal in the process of coking is pre-heated to between 500° and 600° out of contact with air so as to destroy the non-coke-producing substances in the coal and to leave not less than 5% by wt. of the resinic substances. This process is in a vacuum. Cf. 125,379.

Coking. S. R. ILLINGWORTH. Brit. 186,085, March 24, 1921. In the production of smokeless fuel and coke, a blend is made of two coals or of coal and coke, semi-coke, or ore so that the resinic content of the blend is not less than 5% but preferably not less than 8% of the wt. of the blend. This blend is heated to a temp. not exceeding 500°

or to a temp. of from 50 to 100° above the min. temp. at which the resinic matter is destroyed. To increase the contraction of the blend, the volatiles evolved between 350–400° should be below 7.5%. Blended coals may be treated as described in 175,888 (C. A. 16, 2217), that is, first prebeated and then heated to 500° and the product subsequently carbonized at 900–1000°. The products of the process described in 164,104 (C. A. 16, 1312) may form part of the blend.

Coke-oven wall construction. J. GEIGER. U. S. 1,433,450, Oct. 24.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Properties of Texas crudes. J. B. RATHBUN. *Petroleum Age* 10, No. 10, 37 (1922).—A compilation of phys. data on the various Texas crudes including distn. tests. D. F. BROWN

Methods for determining sediment in fuel oils. A. D. BAUER. Bur. of Mines, *Repts. of Investigations* No. 2408, 4 pp. (1922).—The benzene extn. method (C. A. 16, 3199) can be used satisfactorily for all fuel oils. For oils having viscosities above 200 Saybolt Furol at 122° F., the centrifuge method of the Am. Soc. Testing Materials (C. A. 16, 3199) cannot be used, since no clear line of demarcation between the sediment and the benzene is observable. A table gives the results obtained on about 20 fuel oils by the two methods. A method proposed by Dean and Lerch is described. Although the results by the latter method compare satisfactorily with the benzene extn. method, B. does not favor it. An alundum crucible is used, and the difficulty of removing all oil and of keeping the rubber ring (gasket) from contact with benzene soln. render the method tedious. Also in *Refiner* 1, No. 3, 12 (1922). W. F. FARAGHER

Ozonides of petroleum hydrocarbons. RUDOLPH KOETSCHAU. *Z. angew. Chem.* 35, 509–13 (1922).—Ozonides of petroleum are of interest in several ways: they offer possibilities as *resins*, for uses like those of the coumarone resins; their formation and removal from petroleum fractions constitute a possible method of *refining*; and the extent to which they are produced from a crude or fraction is a promising analytical procedure. The possibility of detg. the constitution of some of the constituents of petroleum is emphasized. Several oils were used, among them a transformer oil made from Gulf Coast Crude. The tests of this oil were as follows: sp. gr., 0.915; flash point (closed-cup), 155°; Engler no. at 20°, 6.5 and at 50°, 1.9; cold test, below –20°; mean mol. wt. (by f.-p. lowering of benzene soln.), 293. The ozonides from this oil were made at 12°, and kept in a Dewar flask at –5° to prevent decompn. The yield of ozonides was 25%. When detd. at once, the av. mol. wt. of the ozonides was 663. After the benzene soln. had stood for several hrs., the mol. wt. found was 606, and after 2 days, 479. This behavior is contrary to the statement of Molinari and Fenaroli (C. A. 3, 322) that polymerization occurs in benzene soln. As prepd., the ozonides were white solid or semi-solid substances, insol. in petroleum ether. Unless kept at low temp., they decomposed and became red in color. Ozonides which were kept 1 day at 0° had an av. mol. wt. of 606. When the benzene soln. was allowed to stand for 2 days after the original detn., the value found was 479. Ozonides which stood for 3 days at room temp. had a mol. wt. of 516. If oils are purified with $AlCl_3$, the S content is reduced markedly, and ozonides made from the purified oils are quite stable. The oils were ozonized in Lausiedl potash bulbs, or in a special bulb designed by K. (photographs are reproduced). Detn. of ozone numbers, i. e., the wt. of ozone taken up by an oil under specified conditions, is not recommended by K. since the variations are too large. The absorption of ozone is very rapid at first (2–5 hrs.), and then becomes slower. A

suitable analytical method is as follows: Ozonize samples of oil for 2-5 hrs., and then boil a weighed sample of the product with H_2O for 5 hrs. The acid no. of the ozonized oil is then detd. by the usual titration. Low acid numbers indicate stable oils. The ozonized oil may be treated by the Kissling method for tar-number; the rapidity of the action of ozone being an improvement over the oxygen used by Kissling. The details of the test have not been worked out completely, but preliminary results are promising.

W. F. FARAGHER

Use of sulfur dioxide in treating oils. ANON. *Refiner and Nat. Gasoline Mfr.* 1, No. 2, 22-6(1922).—Numerous charts are given showing the soly. of various hydrocarbons in liquid SO_2 . It is shown that the olefins and aromatics are completely miscible at temps. of -10° and -18° , while the soly. of the paraffins ranges from an unmeasurable quantity at -18° to 1.8% at -10° . Contrary to the work of Edelenau and Browery, it is found that the naphthenes vary in soly. from 0 to 100%, depending upon the temp. and concn. of the liquid SO_2 . A compound is probably formed between the SO_2 and the naphthenes. Various synthetic mixts. of hydrocarbons were treated with liquid SO_2 . It was found that the extn. of aromatics by SO_2 is limited to mixts. contg. less than 50% of aromatics and efficient extn. is possible only below 25% of aromatics. The aromatics may be completely sepd. from the naphthenes if the percentages of the solvent are kept low. Up to 20% olefins may be satisfactorily sepd. from paraffins. In sepg. naphthenes from paraffins by this method the former are recovered and may be used with lubricating oils.

D. F. BROWN

Loss of gasoline by evaporation. J. H. WIGGINS. *Nat. Petroleum News* 14, No. 47, 30-2; No. 48, 29(1922).—A loss from evapn. of crude oil produced in the U. S. in 1922 is now known to have a value of \$250,000,000. Most of this loss can be prevented by using gas tight storage tanks as shown by the following table:

Evapn. losses with tank standing full (250 bbl. tanks contg. very light Osage County oil).

Kind of roof.	Time days.	Av. oil temp. $^\circ F$.	%.	Loss bbls.	Change in density From.	To.	Eq. degrees Drop.
open	12	38	5.35	12.65	38.60	36.17	2.43
4" open vent	12	41	1.21	2.75	38.98	38.62	0.36
Practically tight	12	45	0.26	0.60	39.33	39.26	0.07

Figures are presented to show that gasoline made by preventing evapn. costs \$1.38 per bbl. less than cracked gasoline and is of better quality. An quipment to save 1000 bbl. daily would cost \$392,500 and would show a net annual profit of \$1,730,000.

D. F. BROWN

Refining odors. J. E. HACKFORD. *Oil Eng. and Finance* 2, 573(1922).

D. F. BROWN

Laboratory examination of paraffin and vaseline. E. PYHÄLÄ. *Petroleum Z.* 18, 1164-5(1922).—The sp. gr. of paraffin is detd. by floating in alc.-water mixts. and detg. the sp. gr. of the latter. In measuring the dropping point of vaseline with the Ubbelohde app. it was found that variation in results could be avoided by first melting the vaseline on a glass plate and allowing it to congeal thereon. This has the effect of making it more homogeneous.

D. F. BROWN

The oil shales of Kentucky. V. C. ALDERSON. *Railroad Redbook* 39, 923-7 (1922).—A description of the location and formation of the Kentucky shale deposits is given. It is estd. that 1000 sq. mi. are exposed and available for com. exploitation by open cut and steam shovel methods. The shale has an av. yield of oil of about 16 gal. per ton and has a sp. gr. of 2.173, S content of 1.5 to 4.15, N content of 0.26 to 0.57, moisture content of 0.83 to 1.59, volatile combustible matter from 16.72 to 10.26, fixed C 4.61 to 10.06, ash 75.43 to 83.90%. In addn. Kentucky shale will produce $(NH_4)_2SO_4$ and other products may be developed later.

D. F. BROWN

Forest Products Laboratory. ANON. U. S. Dept. Agr., *Circ.* 231, 1-47 (1922).—A general outline of the aims and scope of work of the Laboratory. W. H. ROSS

Pine oil. ("Liquid rosin," "polytepen," "sulfate resin".) HÅKAN SANDQVIST. *Z. angew. Chem.* 35, 531-3 (1922).—In the production of wood pulp from pine, by the soda process, a dark soap seps. which on acidifying yields about 45 kg. of pine oil per 1000 kg. cellulose. Spruce does not yield this soap. To det. the natural variation in the analytical constants of this oil, samples from different Swedish factories were examd. and results tabulated. On the purified oil av. results are: d_4^{15} 0.99; indifferent substance, 16%; resin acids, 43%; fatty acids, 41%. The indifferent substance is not quite neutral (acid no. 4 to 11), is very viscous, partly crystallizable, d , 0.99 to 1.0, positively rotatory. The crystallizable portion, which makes up about 3% of the oil, is somewhat like phytosterol, m. 136-7°, $[\alpha]_D^{25}$ —190, and formula $(C_{22}H_{34}O)_2$. The acetyl deriv., $C_{24}H_{38}O_2$, m. 122-3°, shows many similarities to Lieberman's cholestol. The liquid portion of the indifferent substance contains considerably more O than $(C_{22}H_{34}O)_2$. The resin acids show d , 1.104; $[\alpha]$, +9, soften at 80-90°, become liquid at 130°. The crystd. acids melt at 158-65°. The fatty acids show d , 0.968, and are optically inactive. Crystals sepd. from the acids had a m. p. 72-3°; hydrogenation produced some stearic acid, indicating oleic and linolenic acids; palmitic acid was not found. Some of the acids no doubt belong to other than the aliphatic series. The technical usefulness of the oil depends on whether fatty and resin acids can be sepd. Distn. increases the proportion of fatty acids and decreases the resin acids, but complete sepn. is not possible. Results of the examn. of distn. fractions are tabulated. Cf. *C. A.* 3, 1697; 6, 2528; 15, 3095. F. A. WERTZ

Apparatus for distilling volatile hydrocarbons from coal, shale or lignite (U. S. pat. 1,432,275) 21. Apparatus for feeding finely divided shale, oil-sand or S ore into retorts (U. S. pat. 1,432,170) 1.

Distilling petroleum. W. C. and F. E. WELLS. U. S. 1,433,052, Oct. 24. Petroleum is passed continuously into a still having its bottom covered with Pb or other heavy inert material which fuses but does not evaporate at the still temp. and distn. is effected under the action of a neutral gas which is passed up through the material in the still and serves to sweep off the constituents in the order of their volatility. Vapors evolved are passed through a fuller's earth filter mounted on the still and are thence led to a condenser. Uncondensed gases are returned to the still to repeat the cycle of operation.

Distilling oil shales. P. DANCKWARDT. U. S. 1,432,101, Oct. 17. Highly heated waste shale or rock (carrying C) and fresh shale are charged into and mixed together within a vertical cylindrical distg. chamber so that the heat from the waste shale serves to effect distn. of volatilizable values from the fresh shale. Waste shale is continuously withdrawn from the lower portion of the distg. chamber.

Distilling oil from shale or other solid materials. W. C. and F. E. WELLS. U. S. 1,433,051, Oct. 24. Shale or similar material is continuously passed into an annular columnar retort both sides of which are heated by combustion gases. A neutral heated gas is introduced into the lower end of the retort and serves to liberate vapors which are led off from a middle zone of the retort.

Apparatus for petroleum distillation. E. W. ISOM and J. E. BELL. U. S. 1,432,067, Oct. 17. A horizontal drum for cracking petroleum is connected in a circulating oil system with a heater, and a pump between the drum and heater is so mounted as to move freely with expansion and contraction of the connecting piping.

Apparatus for separating oil from gas. K. L. REYNOLDS. U. S. 1,432,208, Oct.

17. The app. is especially adapted for treating the gas and liquid products flowing from oil wells.

Filtering petroleum oil vapors. W. C. and F. E. WELLS. U. S. 1,433,050, Oct. 24. Oil is distd. by passing a neutral gas through it in a still and the vapors evolved are filtered through fuller's earth or a similar decolorizing agent.

Glucose and dextrin from wood. H. TERRISSE and M. LEVY. Brit. 186,139, June 20, 1921. Addition to 143,212 (C. A. 14, 2870). Wood is treated first with liquid and then with gaseous HCl and spread into thin layers and allowed to digest. The resulting material is of a loose powdery texture so that the acid can easily be extd. from it. A suitable construction is specified.

23—CELLULOSE AND PAPER

CLARENCE J. WEST

Some physical properties of cotton cellulose and its modifications. A summary of existing data. GEO. E. COLLINS. *J. Text. Inst.* 13, 204-13(1922).—The literature is assembled for the following properties: sp. gr., elasticity, sp. inductive capacity, electrification, mech. adsorption of liquids, thermal effects accompanying adsorption, action of heat and cold, thermal cond., sp. heat, heat of combustion and of reaction, refractive index, double refraction, action of ultraviolet light, optical activity of sols, ultramicroscopy, evidence of X-rays on structure. 87 references are quoted.

C. J. WEST

Oxycellulose; its formation and reactions. A summary of the literature. PERCY H. CLIFFORD and ROBERT G. FARCHER. *J. Text. Inst.* 13, 189-204(1922).—A review of the methods of oxidation of cellulose and of the reactions of and tests for oxycellulose. Ninety references are given. Also in *Am. Dyestuff Rep.* 11, 405-27, 427-30 (1922).

C. J. WEST

Modern methods of wood pulp manufacture. GUSTAV HELLSTROM. *World's Paper Trade Rev.* 78, 1492, 4, 6, 8, 1500(1922).—An address, in which is reviewed the sulfite and sulfate processes, bleaching, treatment of the spent liquor, including the Rinman process.

C. J. WEST

Paper drying and production. G. A. JAHANS. *World's Paper Trade Rev.* 78, 1570, 2, 4(1922).—Better results in drying paper are obtained by maintaining the 1st 4 of a series of 24 cylinders at 30°, the last 4 at 120° and distributing the temp. difference between the remaining 16 cylinders. In 50% of the cases the paper thus prepd. was stronger in machine and cross direction, the production was increased 15-20%, and in some cases at least, less steam was consumed.

C. J. WEST

Action of the heater in paper making. SIGURD SMITH. *World's Paper Trade Rev.* 78, 1705-10, 1810-6(1922).—Largely a discussion of the mech. features of heating as outlined in S.'s recent book. The *Duplex heater* is described; this is provided with 2 hedplates located under the roll and sepd. by a wide gap or chamber. This heater gives twice the output of the ordinary heater and at the same time saves 25% in power when handling rags or 33% when handling chem. wood pulp. Also in *Paper Trade J.* 75, No. 26; 76, No. 1(1922-23). *J. Roy. Soc. Arts* 71, 38-53(1922).

C. J. WEST

Paper for books. R. W. SINDALL. *Paper Makers' Mo. J.* 60, 413-8; *World's Paper Trade Rev.* 78, No. 20, 1682(1922).—The following conditions are laid down for suitable book papers: Esparto and chem. wood pulp in any convenient proportions; mineral matter should not exceed 15%; thickness should not exceed 0.125-0.150 mm. (0.005-0.006 in.); the pulp should be beaten so as to give a close, dense sheet of max.

strength. The life of a book may be prolonged by making the machine direction of the paper parallel with the width of the book. Supercalendered imitation art papers may be used in place of art papers.

Rubber latex in paper making. F. KAYE. *World's Paper Trade Rev* 78, No. 18, 1428; no. 19, 1540(1922); cf. C. A. 16, 4062.—General discussion of the application of rubber latex to various kinds of papers and boards. The only serious problem in its use is to find the best condition of diln. and when and how to add to the beater. The latter may depend upon the nature of the fiber and degree of hydration it has already reached or is desired. The effect of different coagulants upon the strength of the resultant papers is a matter for expt. $MgSO_4$ appears to be a suitable material.

C. J. WEST

Viscous cellulose ether composition. W. R. WEBB. U. S. 1,432,373, Oct. 17. Viscous compns. adapted for making films are formed of cellulose ethyl ether, ethylene chlorohydrate and MeOH or EtOH. U. S. 1,432,374 relates to similar compns. prepd. from cellulose ethyl ether, MeOAc and MeOH with or without other modifying compds.

Cellulose ether composition for films. R. L. STINCHFIELD. U. S. 1,432,364, Oct. 17. Cellulose ethyl ether is formed into a viscous soln. with $C_2H_5Cl_4$ and MeOH or EtOH. U. S. 1,432,365 relates to similar compns. contg., as additional ingredients, esters such as MeOAc or EtOAc.

Comminuting pitch. F. J. COMMUN. U. S. 1,432,742, Oct. 24. Coarsely ground pitch is treated in a ball mill with an equal wt. of H_2O and about 2% of a resin soap, to obtain a finely dispersed product adapted for admixt. with cellulose pulp.

Asbestos paper. N. SULZBERGER. Brit. 186,409, June 24, 1921. Non-charring asbestos paper, etc., is made by using an inorg. colloid as a binder or, if an org. binder is used, the org. matter is removed by beating under oxidizing conditions. As colloid, Al silicate may be used (with NH_3 and tannic acid), or $BaSO_4$. Where an org. binder is used, the paper is preferably also treated with an oxidizing agent such as nitrocellulose or a soln. of saltpetr. A small amt. of catalytic material which promotes oxidation may be added. The asbestos paper may serve as a carrier for catalytic material, such as finely divided Pt, for making fireproof fabrics such as cloth and lace, for gas mantles, or for insulating material. It may be used for cigaret wrappers and bolders for cigars and cigars may be made therefrom. When used for cigaret wrappers, the presence of an oxidizing agent such as saltpeter in the paper promotes the combustion of the tobacco during smoking.

Coating paper webs. F. P. REED. U. S. 1,432,734, Oct. 17. One face of a paper web is moistened, and coloring matter is applied to the moistened face in streaks followed by printing of an overlying printed design. The pat. also covers a machine for carrying out these successive operations.

Apparatus for washing and screening paper stock after delivery from a digester. F. P. MILLER. U. S. 1,432,774, Oct. 24.

Rosin sizing. J. A. DECEW. U. S. 1,433,124, Oct. 24. Rosin for use in sizing paper is incorporated with 5% of rubber by use of a common solvent such as gasoline which is afterward evapd.

Removing ink from paper. H. R. EYRICH and J. A. SCHREIBER. Brit. 186,372, May 17, 1921. In removing ink from paper, colloidal material such as bentonite, having over 50% of its particles of diams. less than 0.0015 mm., or more than 70% colloidal, is used. A mixt. of cut or beaten paper, alk. material such as Na_2CO_3 , and bentonite or the like, is agitated in running H_2O . The paper material is held by a screen while the water carries off the bentonite or the like and ink. The material is then neutralized

with an acid or acid salt, such as NaHSO_4 or $\text{Al}_2(\text{SO}_4)_3$, and thus brightened. The material may then be sized, dyed to give it the right shade, and then mixed with pulp and re-made into paper. Cf. C. A. 16, 2990, 3394.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Use of wood distillation products in the dye industry. H. M. BUNBURY. *Chem. Age (London)* 7, 598-9(1922).—The uses of AcOH , CH_3CICOOH , acetoacetic ester, $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$, MeOH and HCHO in the manuf. of dyestuffs are described, also the uses of AcOH , various metallic acetates, pyroligneous acid, red liquor, and black or iron liquor in the processes of dyeing. All of these substances are derived directly or indirectly from the crude acid and crude MeOH produced by the distn. of wood. L. W. R.

Mordants. III. Chrome. W. D. BANCROFT. *J. Phys. Chem.* 26, 736-72 (1922); cf. C. A. 16, 4067.—Wool adsorbs $\text{H}_2\text{Cr}_2\text{O}_7$ from dichromate soln. and this is reduced to Cr_2O_3 which is the mordant. Within limits the adsorption of $\text{H}_2\text{Cr}_2\text{O}_7$ is increased by increasing the acid concn. $\text{H}_2\text{Cr}_2\text{O}_7$ oxidizes org. acids more readily in the presence of wool. H_2SO_4 is more effective than HCl or HNO_3 in causing the oxidation of wool by $\text{H}_2\text{Cr}_2\text{O}_7$. There is no appreciable oxidation of wool when oxalic, lactic, or formic acid is used as an assistant. A basic sulfate is first formed when wool is mordanted from chrome alum; but the former changes later to Cr_2O_3 . Silk adsorbs Cr_2O_3 less strongly than wool. Cotton takes up no Cr_2O_3 from chrome alum but it adsorbs it from an alk. soln. There is no evidence of any definite compd. being formed when wool is mordanted with Cr_2O_3 . HARRY B. WEISER

The mordanting of wool with potash alum. W. W. PADDEN. *J. Phys. Chem.* 26, 790-3(1922).—The mordanting of wool with potash alum does not lead to the formation of definite chem. compds. on the fiber but it is strictly an adsorption phenomenon involving both Al_2O_3 and H_2SO_4 . HARRY B. WEISER

Fastness of dyeings to gases. E. RISTENPART AND P. WIELAND. *Textilber.* 3, 397(1922); cf. Heermann, C. A. 16, 2406.—If the fuchsin-sulfurous acid method for the detection of HCHO is used, as recommended by Heermann (*l. c.*) a blank should be run to prove the condition of the reagent, since it is very unstable. R. and W. recommend that the sample of the dyeing shall not be placed into the soln., since other things than HCHO may affect the reagent. Removal of HCHO by steam distn. and examn. of the distillate are preferable. Four dyes submitted for test of fastness to HCHO were found satisfactory when examd. singly. Mixts. of pairs, however, were faded. It is suggested that HCHO is a potentially unsatd. substance, $\text{H}_2\text{C}=\text{O}$, which can couple 2 mols. of unsatd. dyes through the agency of its 2 free valencies. Two like mols. of some dyes may resist this action, whereas a mol. of this dye and one of another which is also fast when alone may be coupled. The remedy for the defective dyeings encountered frequently is to avoid the use of finishing or packing materials which contain HCHO . W. F. F.

Manufacture of artificial silk. REX FURNESS. *Chem. Age (London)* 7, 522-4(1922).—The nitrocellulose, cuprammonium, cellulose acetate and viscose processes are described with emphasis on the latter process. The recent use of metallic thiocyanates as cellulose solvents is discussed and many suggestions are given for the dyeing of artificial silk. L. W. RIGGS

Modern flax industry. Technical requirements of bast fiber retting. F. TONLER. *Z. Ver. deut. Ing.* 66, 931-3(1922).—Flax retting is carried out by allowing the stalks to come in contact with water, either in slow running streams, pits, or pools for 1-4 weeks. In this way microorganisms are given an opportunity to act. After the retting

is completed the flax is removed from the water, spread out and allowed to dry in the air. The flax can now be separated from the stalks by beating. Until recently little progress has been made in scientific control of this industry. Expts. have been made of introducing bacteria into the pool or pit to assist in the process of retting. Conclusive results are not yet available from these expts. C. T. WHITE

Machines for flax manufacture and production. W. MÜLLER. *Z. Ver. deut. Ing.* 66, 984-7 (1922).—A description is given of the various machines used in the flax industry. C. T. WHITE

Cottonizing of flax and hemp wastes. P. WARNTIG. *Z. Ver. deut. Ing.* 66, 987-9 (1922).—Waste flax, hemp, and certain less desirable grades of flax which have formerly been considered as waste may be treated chemically and the fibers sepd. from the lignin. The fibers thus obtained are used either with cotton or in the case of flax in the manuf. of linen. The following methods are some of the most important for the sepn. of the lignin: (1) treatment of raw material with any one of the following, NaOH, KOH, NH₄OH, Ca(OH)₂, Mg(OH)₂, or Na₂S, with or without pressure and at varying temp. Org. solvents may also be used. (2) Treatment with NaHSO₃. (3) Treatment first with acid, then alkali or *vice versa*. (4) Treatment with Cl₂. (5) Mech. sepn. after long period of retting, which has been followed by bleaching. Choice of method depends to a great extent on availability of app. and necessary chemicals. C. T. WHITE

Anthraquinone (BATTEGAY) 10. Certain triphenylmethane dyes (JACOBS, HEIDELBERGER) 10. Optically active dyes. I. (INGERSOLL, ADAMS) 10. Some physical properties of cotton cellulose and its modifications. A summary of existing data (COLLINS) 23.

Dyes. BRITISH DYESTUFFS CORPORATION, LTD., J. BADDILEY, J. B. PAYMAN and E. G. BAINBRIDGE. Brit. 185,880, June 23, 1921. Direct dyeing cotton dyestuffs of the tartrazine type are obtained (a) by condensing 2 mol. proportions of an arylbenzothiazole hydrazine with 1 mol. proportion of dihydroxytartaric acid, (b) by coupling a diazoarylbenzothiazole with a pyrazolone derived from an arylbenzothiazole and acetoacetic or oxalacetic ester. The products dye cotton orange shades fast to light and washing.

Dyes; intermediate products. BRITISH DYESTUFFS CORPORATION, LTD., J. BADDILEY, E. H. RODD and H. H. STROCKS. Brit. 186,517, Sept. 14, 1921. Triaryl-methane dyes contg. a thiazole ring are prepd. by condensing a tetraalkyldiaminohenzohydrol with an arylbenzothiazole and oxidizing the resulting leuco compd. Examples are given. The products dye wool or tannin-mordanted cotton and also unmordanted cotton or paper, bright green shades.

Dyes; dyeing and printing textiles. DURAND ET HUGUENIN, SOC. ANON. Brit. 186,057, Sept. 11, 1922. Reduction products of vat dyes (indigo, thioindigo, indanthrene, etc.) are converted into enolic esters, which are stable in air, by the reaction of acids with the hydroxyl groups of the reduction products. Animal or vegetable fibers are dyed or printed with these compds., which are converted on the fiber into the dyestuffs by hydrolysis and oxidation, or by oxidation only.

Dyeing loose fibrous material. JOHN, THOS., and JOS. BRANDWOOD. U. S. 1,432,318, Oct. 17. Loose cotton or other fibrous material is passed on a belt in close contact with a perforated cylinder through which dye liquor is supplied. U. S. 1,432,319 relates to an app. for effecting a similar treatment.

Dye vat and dye liquor circulating devices. J. D. HENON. U. S. 1,432,276, Oct. 24.

Waterproofing cloth. C. BIONDO. U. S. 1,432,833, Oct. 24. A waterproofing

soln. is formed by adding to 10 liters of hot H_2O 1 lb. Na_2CO_3 , 1 oz. castor oil and 1 oz. oil of turpentine and then stirring in 2 lbs. of alum. After dipping in this soln. the cloth is dried and then washed.

Degumming silk. S. A. WAKSMAN. U. S. 1,432,312, Oct. 17. Degumming is effected by the action of strongly proteolytic bacteria.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

The chemistry of varnishes and its relation to colloid chemistry. HANS WOLFF. *Z. angew. Chem.* 35, 555-7(1922).—A review. Cf. *C. A.* 14, 2092; 16, 2232. F. A. W.

Old experiments on anti-fouling paints. N. H. ADAMSON. Paint Manufs. Assoc. of U. S., *Circ.* 156, 15-34(Oct., 1922).—A review of the U. S. Navy's research on ship bottom paints. The best anti-corrosive results were obtained with a shellac varnish paint contg. some turpentine, pine oil, ZnO , and Zn dust; and the best anti-fouling results, with a similar paint contg. dry Indian red and HgO instead of Zn dust. Oil and varnish vehicles dry too slowly and are not effective. Powdered SiO_2 is a good pigment for anti-corrosive paints; and blanc fixe for anti-fouling paints. Results of the inspection of paints contg. a variety of toxic pigments, and vehicles, are tabulated.

F. A. WERTZ

The present status of research on lithopone. E. MAASS AND R. KEMPF. *Z. angew. Chem.* 35, 609-11(1922).—Brief historical and production statistics on various white pigments are given. The deficient resistance of lithopone paints to weather is variously ascribed to gradual transformation of the amorphous pigment to the crystal line form; spontaneous increase of the pigment particle size during exposure; lack of formation of the highly durable heavy metal soaps by reaction with the vehicle, as is the case with white lead and ZnO ; transformation of ZnS into $ZnSO_4$ through the action of superoxides formed in linseed oil vehicles. None of these hypotheses explains all the observation on the lack of durability of lithopone paints. Hypotheses for the cause of the gray discoloration of lithopone on exposure to light, and the hiding power and oil absorption properties of the pigment are briefly reviewed.

F. A. W.

The scope of the work of the Research Laboratory for Paint Technology (Versuchsanstalt für Maltechnik) at the Munich Technical High School. A. REISNER. *Farben-Ztg.* 27, 3321-3, 3377-9; 28, 33-5, 108-9, 182-4(1922). F. A. WERTZ

Fine industrial lacquers. FR. ZIMMER. *Z. deut. Öl-Fett-Ind.* 42, 696-8(1922).—German "lacquers" are varnishes that contain some solvent—in distinction from "Firniss" lacquers which represent boiled oil varnishes. The article describes the uses and application of 2 main classes: (1) alc. lacquers, which contain Me, Et, or amyl alc., amyl acetate, acetone, ether, or sometimes a little benzine or benzene as a solvent, and (2) cellulose lacquers, which have amyl acetate, acetone, MeOH, ether, AcOH, etc., as solvent. "Zapon" lacquers contain nitrated cellulose and "Cellinn" lacquers contain acetylcellulose as a base. Some details are given about their use.

P. E.

Industrial application of the colloid mill. S. P. SCHOTZ. *Chem. Age (London)* 7, 493-5(1922); cf. *C. A.* 16, 2745.—Application of the colloid mill in the varnish industry (1) does away with gum running, (2) allows almost unlimited choice of solvents for substances formerly requiring particular media, (3) admits application of new materials, and (4) permits the use of fillers for specific purposes. Applications to the paint and the superphosphate industries are briefly outlined.

W. H. B.

Artificial resins. H. C. RAUCH. *Z. deut. Öl-Fett-Ind.* 42, 709-10(1922).—

A brief survey of the manuf. of various shellac substitutes that have been developed in Germany on account of the high price of shellac, including resins obtained by polymerization of single compds. such as coumarone, furfural, and aldehyde resins; by hardening natural resins by metallic oxides; by oxidation or esterization; and by condensation of several chem. compds. with subsequent polymerization, such as phenol-, aniline- and naphthalene-formaldehyde resins.

P. ESCHER

Ozonides of petroleum hydrocarbons (KORYSCHAU) 22. Powdered carbonaceous char (U. S. pat. 1,433,039) 18.

Paints. IMPERIAL TRUST FOR THE ENCOURAGEMENT OF SCIENTIFIC & INDUSTRIAL RESEARCH AND S. B. SCHRIVER. Brit. 186,156, June 21, 1921. Washes, distempers, and water paints are made from the proteins obtained from castor beans or other oil-bearing seeds. The proteins are mixed with alkalis, such as NaOH or alk. carbonate, or a substance such as NaF which reacts with slaked lime to form NaOH, together with slaked lime or MgO, to form cement-forming material. The cement-forming material is mixed with pigments which resist the action of alkalis, and H₂O is added. The resulting jellies, on standing, become semi-liquids capable of direct application as distempers. The pigments used include ZnO, lithopone, whitening, ultramarine, burnt sienna, and Brunswick green. The preferred proportions are 4 parts of cement-forming material to 30 parts of other material.

White lead. A. E. WHITE. Brit. 186,114, June 14, 1921. Pb is continuously agitated in presence of CO₂, air and dil. HOAc; the addition of the liquid reagent is so controlled that the mass under treatment is always somewhat moist, but never so moist as to be pasty. A suitable construction is specified.

Varnish. J. H. YOUNG. U. S. 1,432,511, Oct. 17. Resin is uniformly heated in a closed vessel by oil of high h. p. or other heating medium in a jacket around the vessel and heated varnish oil is added to the melted resin in the vessel. The mixt. is cooked in the vessel, then partially cooled by lowering the temp. of the heating medium in the jacket, mixed with a thinner and more rapidly cooled.

Vehicle for paints or varnishes. S. LERNER. U. S. 1,432,110, Oct. 17. Melted rosin 4 lbs. is allowed to cool for a few min., and mixed with 10% of a mixt. formed from 1 pint each of turpentine, petroleum ether, rosin spirit and coal-tar naphtha. This mixt. is allowed to cool to about 10°; 1 pint of benzine is slowly added to it and the remaining 90% of the mixt. of turpentine, etc., is then added. The product is adapted for use as a substitute for linseed oil.

Synthetic resins. SOC. ANON. POUR L'IND. CHIM. A BALE. Brit. 186,107, June 9, 1921. Resinous products are obtained by heating phenols with S in the presence of a base in an amt. not more than 1/5 equiv. of the phenol; 2-3 atoms of S per mol. of phenol are used and the heating is continued until evolution of H₂S ceases. Catalysts such as halogens or compds. yielding halogens may be added. The products are fusible and sol. in alkalis, alc., acetone, or benzene, and may be converted into insol. infusible products by prolonged heat, or heat and pressure, or they may be hardened by treatment with a small amt. of HCHO or substances yielding it.

27—FATS, FATTY OILS, WAXES AND SOAPS

R. SCHERUBEL

The relations between fat constants. JACOB LUND. *Z. Nahr. Genussm.* 44, 113-87(1922).—In slightly different form, this paper has been published previously in Norwegian. See C. A. 8, 1516. D. B. DILL

Microbic fat production, with special consideration of *Endomyces vernalis*. P. LINDNER. *Chem. Umschau* 29, 343-4(1922).—All sugars except lactose and xylose are suitable as nutritive media for *Endomyces vernalis*, yielding varying amts. of fat according to the nature of the sugar. Most N decompn. products except guanidine and betaine may serve as a source of N. When sulfite liquor is used as a medium other carbohydrates in it besides sugar are also utilized. Kelp, with its enormous surface area and its high content of mannitol, K_2O and P_2O_5 , should prove an excellent medium. The yield of fat is shown by Deutschland's expts. in which 1 cu. m. of liquor to which 1.33 kg. of basurol and some K_2O and P_2O_5 had been added, furnished after 6 days 10.08 kg. dry solids, contg. 4.51 kg. of fat, equal to 44.72%. Ordinary beer yeast and also butyric acid bacteria produce considerable fat in the presence of sugar and much O . Tuberculosis bacilli are readily fattened and may possibly be destroyed by carrying the process to its end, as shown by *Antomyces renkuffii* Grüss which is killed within 24 hrs. by its fat production. Attention is also called to the production of fat by many of the lower organisms such as bread-bug, fly-larva, etc. If *E. v.* is left to autodigestion, the N products leave the cell and the fat coalesces into globules within the cell which facilitates extr. by solvents. P. ESCHER

Chemical composition of soy bean oil. W. F. BAUGHMAN and GEO. S. JAMIESON. *J. Am. Chem. Soc.* 44, 2947-52(1922).—The oil had the following consts.: d_{40}^{25} 0.9203- n_{20} 1.4739, I no. (Hanus) 128.0, sapon. value 189.5, acid value 0.5, Ac value 17.0, Reichert, Meissl no. 0.16, Polenske no. 0.26, unsaponifiable matter 0.6%, satd. acids (detc.) 12.7, unsatd. acids + unsaponifiable matter (detc.) 83.0, satd. acid (cor.) 11.5, unsatd. acids (cor.) 83.5, I no. of unsatd. acids 148.7. It consists of the glycerides of the following acids: linolenic 2.3, linolic 51.5, oleic 33.4, palmitic 6.8, stearic 4.4, arachidic 0.7, lignoceric 0.1%. C. A. R.

Chemical composition of sunflower-seed oil. GEO. S. JAMIESON and W. F. BAUGHMAN. *J. Am. Chem. Soc.* 44, 2952-7(1922).—The oil had the following consts.: d_{40}^{25} 0.9193, n_{20} 1.4736, acid value 2.3, I no. (Hanus) 130.8, sapon. value 188.0, Ac value 14.5, Reichert-Meissl no. 0.27, Polenske no. 0.25, unsaponifiable matter 1.20%, I no. of unsaponifiable matter 124.8, satd. acid (detc.) 7.4%, I no. of satd. acids 5.0, unsatd. acids + unsaponifiable matter (detc.) 87.5%, I no. of unsatd. acids + unsaponifiable matter 147.5, I no. of unsatd. acids 147.9, satd. acids (cor.) 7.1%, unsatd. acids (cor.) 80.6. It consisted of the glycerides of the following acids: oleic 33.4, linolic 57.5, palmitic 3.5, stearic 2.9, arachidic 0.6, lignoceric 0.4%. C. A. R.

Brazilian oil fruits. CL. GRIMME and R. KAYSER. *Z. deut. Öl-Fett-Ind.* 42, 614-7(1922).—I. Palm fruits. A systematic study of Brazilian oils was undertaken with a view of cultivating Brazilian oil fruits. The following palm fruits were examd. and the results tabulated, with description of plants, statistics on crops, etc.: (1) Cayana, *Elaeis melanococca* Mart.; (2) *Astrocaryum Jansary* Mart.; (3) Tucuma, *Astrocaryum tucuma* Mart.; (4) Muru-muru, *Astrocaryum murumuru* Mart.; (5) Inaya, *Maximiliana regia* Mart.; (6) Babassee, *Orbignia martiana* Barb. Rodr.; (7) Uruahy, botanically undetermined. The oil content of the kernels varies from 21.1% for (2) to 63.84% for (6). P. ESCHER

The modern toilet soap factory. GEORG ILIERT. *Chem. App.* 9, 207-10(1922).—

A description of a practically automatically operating factory, with 8 cuts of app., including a plan and elevation showing the arrangement of the app. for drying, mixing, cutting and pressing.

J. H. MOORE

The determination of chlorides in soaps. ROBT. JUNCKUNZ. *Seifensieder Ztg.* 49, 706-7(1922).—J. points out the inadequacy of the methods for Cl detn. in soaps as given in the literature, discusses in detail the methods of Mohr, Volhard and Bennett, and describes his own procedure, based upon expts. with soaps of known NaCl content. Five g. of the soap are dissolved in about 40 cc. H_2O in a 200 cc. flask, 5 cc. of concd. HNO_3 are added to liberate the fatty acids and 25 cc. of 0.1 N $AgNO_3$ are immediately added, with warming to coagulate the ppt. The soln. is cooled, made up to mark and filtered; 100 cc. are titrated back with KCNS and ferric alum indicator. A comparison of this with Bennett's method shows high figures for the latter, probably because it is intended for neutral solns., while most soap solns. are alk., especially soft soaps and washing powders, thereby causing erroneous results. J. suggests that the Cl content of soft soaps be expressed as KCl and that the max. content of NaCl for hard soaps be placed at 2%.

P. ESCHER

Study of catalytic actions at solid surfaces. VIII. The action of sodium carbonate in promoting the hydrogenation of phenol (ARMSTRONG, HILDITCH) 2. Odorless and colorless soy-bean flour (U. S. pat. 1,433,168) 12.

Increasing the consistency of oils. H. MEYER ZU EISSEN (GEN FRENTUP) AND P. KIEDERICH. To mineral and other oils and fats are added a saponifying agent and a product obtained by partly splitting two or more fats or oils with sulfoaromatic acids. These fats or oils are preferably split to an extent of not more than 50%, the resulting mixt. of substances being used without any sepn. Only one of the oils may be split by means of sulfoaromatic acids, the other one being split by any other reagent. One of the two oils is preferably castor oil.

Apparatus for distilling solvents from oils. P. PARODI. Brit. 186,329, Sept. 12, 1922. A column of hollow metal steam-heated disks having inclined surfaces surmounts a series of disks having intervening annular plates. Steam is passed through the disks from an inlet to an outlet. The soln. to be distd. is fed by a pipe and passes in a zigzag course over the upper surfaces of the disks and then over the disks and intervening baffles. Steam is introduced into the lower part of the column by a pipe. A cooling coil may be arranged near the outlet for the oil. Vapors pass upwards around the outsides of or through the centers of the disks to an outlet. The app. may be maintained under reduced pressure. The column and series of disks may be arranged in sep. casings and the liquid from the base of the column may be pumped to the top of the series of disks. The disks are coated with a metal which is not attacked by the solvent.

Nickel catalyst. A. W. CHASE and W. B. VAN ARSDEL. U. S. 1,432,668, Oct. 17. Pptd. $NiCO_3$ is calcined to destroy the gel form, washed to remove sol. impurities and the Ni oxide thus obtained is dried and reduced with H to obtain a catalyst adapted for use in hydrogenating oils.

Revivifying nickel catalysts. G. A. RICHTER and W. B. VAN ARSDEL. U. S. 1,431,982, Oct. 17. Ni catalysts such as those which have been used for hydrogenation of oil are treated with C_6H_6 or other oil solvent and after removal of the oil the spent catalyst is treated with a reagent such as dil. HCl, NH_3 , or lactic or formic acid which will dissolve the oxide film, washed and treated with oil, alc., acetone, H or CO_2 to prevent access of air.

Antiseptic soap. R. MACPHERSON and W. E. HEYS. Brit. 186,078, March 15,

1921. An antiseptic and insecticidal compd. comprizes soap, alkali benzoate, and vegetable or mineral tar.

Soap powder. A. MACLENNAN. Brit. 185,823, June 9, 1921. Fifty-three and one half parts by wt. of a mixt. of equal parts of palm oil and coconut oil are saponified with 31.5 parts of Na_2CO_3 , and 15 parts of H_2O at $33-45^\circ$; excess moisture is evapd. and the cooled solid product is ground. Ultramarine 2% may be added. To remove ink, iodine, paint, or other stains from fabrics, the stain is treated alternately with a soln. of the powder and a 5% soln. of H_2O_2 .

Liquid soap. F. L. EMMERT. U. S. 1,432,102, Oct. 17. An aq. soap soln. is passed through a filter formed of tripoli in order to clarify it for surgical use.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

A new process of purification of cane juice for carbonatation, sulfitation and defatation factories. D. J. W. KREULEN. *Chem. Weekblad* 19, 458-61(1922).—An improvement is described relating to the manuf. of cane sugar in the Dutch Indies. While, so far, the milk of lime is mixed with juice rather slowly, K. has constructed a special app. which sprays the milk of lime into juice by compressed air. In this way decompn. of a part of the sugar by a temporary excess of lime is avoided. The milk of lime must be sieved carefully before entering the app. R. BRUNER

Ash analysis in cane sugar and molasses. H. A. COOK. *Hawaiian Planters Record*, Oct. 1922; *Facts About Sugar* 15, 418-19(1922).—Gives the results of expts. to find a more accurate factor for converting sulfated ash to carbonated ash. It is concluded that the factor of 0.9 in general use is in error and that for sugars there is quite a wide variation for the factor in different samples. For molasses the factor has a relatively const. value. The loss by volatilization in the method of simple incineration is shown to be almost negligible. It is recommended that for ash detns. in all sugar work the method for carbonated ash be adopted. It is suggested that a factor of 0.75 be adopted for molasses. N. KOPPELOFF

Determination of gums in sugar products. H. T. RUFF and J. R. WITHROW. *J. Ind. Eng. Chem.* 14, 1131-3(1922).—Detn. of gums is important as they affect sugar recovery. Of the various methods proposed, pptn. with HCl -alc., CaCl_2 -alc., FeCl_3 followed by alc., and $(\text{AcO})_2\text{Ph}$ -alc., only the first gives satisfactory results which are, however, not abs., but only comparative. When the alc. concn. is kept const., increasing amts. of HCl first give rapidly decreasing results, but after a certain concn. of HCl is reached, the wt. of the ppt. becomes const.; the ash in the ppt. also ceases to decrease. With the acid concn. const., changes in alc. concn. have a marked effect, and a definite % must be adhered to. The following method is recommended: Dil. or conc. the sample to about 50% solids, and centrifuge or filter to remove suspended matter. BzONa may be used for preserving the sample. Weigh or measure into a 120 cc. beaker or Erlenmeyer 20 cc. (or 10 cc., according to expected gum content) of sample, and add 1 cc. (0.5 cc.) of concd. HCl . Slowly run in, under const. agitation, 100 cc. (50 cc.) alc. EtOH of 93-5% is best. In some cases MeOH or even denatured alc. can be used, but then a large supply of these should be kept on hand to get comparative results. Let stand for 15 min., filter through Gooch with 0.2 g. asbestos mat, or alundum crucible. Wash with alc. of full strength; a little acid added sometimes facilitates washing. Dry at $100-5^\circ$ for 1 hr. or to const. wt. Weigh to 0.1 mg., ignite, weigh again, and correct for loss in wt. of crucible. The difference between the two wts. is gums. F. W. Z.

Color and ash absorption by boneblack and decolorizing carbons. W. D. HORNE.

J. Ind. Eng. Chem. 14, 1134-6(1922).—The various carbons now on the market differ from boneblack by their failure to absorb ash, although they are better decolorizers. In order to det. the source of the ash absorption by boneblack, a sample of the latter was split into its two principal components. The mineral portion was isolated by igniting at a low red heat, and the C portion by digestion with HCl, followed by washing. The C was found to be mostly responsible for the decolorization, while the mineral component is the principal ash absorbent. From a simple calen. the conclusion is drawn that under present conditions decolorizing C cannot compete with boneblack for sugar refining, at any price. However, H. has prepd. a filtering medium, in which active C is deposited on a mineral skeleton. This material absorbs ash to a considerable extent. Further work in this direction appears promising.

F. W. ZERBAN

Liquid measure in the sugar industry. A. NEUBURGER. *Deut. Zuckerind.* 48, 579(1922).—Two tanks are provided with floats which actuate a tipping trough, foot valves, and a register, in such a way that as one tank fills the other empties and the no. of times each tank is filled is recorded. With H_2O an accuracy of 0.5% is claimed and with heavy liquids, an accuracy of about 1%.

N. S. V. M.

A new depolymerization product of starch (PICTET, JAHN) 10. Glucose and dextrin from wood (Brit. pat. 186,139) 22.

Recovering litharge from sugar residues. A. S. RAMAGE. U. S. 1,433,034, Oct. 24. Sugar residues contg. $PbCO_3$ and other Pb nonsugars are continuously passed through heating tubes within a furnace while subjected to a continually increasing temp. and to the action of a countercurrent of air of gradually reduced O content. Metallic Pb is first formed which is then oxidized to PbO with the increase of temp. and of amt. of O present.

29—LEATHER AND GLUE

ALLEN ROGERS

Report of the Commission of the French Section of the Society of Leather Trades' Chemists on the Quantitative Analysis of Tanning Materials. M. G. HUGONIN. *Cuir* 1922, 457-64, 484-90.—The principles of the official method are accepted. While not strictly scientific, the lack of knowledge of the chem. constitution of the tannins and of the theory of tannage militate against any radical change unless made on solid grounds. The commission limited itself to the obtaining of the closest possible agreement by the official method. Five analysts examined the following exts.: liquid chestnut, hot sol. quebracho, cold sol. quebracho, mimosa bark, sumac, and mangrove. Detailed instructions were issued for nature of app., reagents, and methods. Special investigation was made of (a) preparation of soln. for analysis, slow cooling overnight and rapid cooling; (b) filtration, with S. and S. 605 and Durieux 111 blue band filter papers, by European and American methods; with Berkefeld, Baird and Tatlock, and Chamberland filter candles; (c) detannization with hide powder chromed with semi-basic $CrCl_3$, semi-basic Cr alum, and normal Cr alum, respectively. It is concluded that (a) the standardization of app. and specification of reagents and details of methods is essential; (b) S. and S. 605 paper is preferable to the Durieux; (c) Berkefeld candles are better than the others, (d) filtration and cooling should both be rapid; (e) basic $CrCl_3$ is preferable for chroming hide powder. Future work will cover the effects of hydron concn. and swelling of hide powder on the sorption of tannin, and also solid exts. and natural materials. The concordance between the different analysts is considered satisfactory. (Deviations

from the mean in non-tans sometimes amounted to 10 percent.—ABSTR.)

F. L. SEYMOUR-JONES

Effect of hydrogen-ion concentration upon the analysis of vegetable tanning materials. J. A. WILSON AND E. J. KERN. *J. Ind. Eng. Chem.* 14, 1128-9(1922).—The % of tannin in quehracho ext. indicated by the A. L. C. A. method increases with p_H value to a max. at 8 and then decreases rapidly, but p_H value has no effect on the detn. by the Wilson-Kern method over the p_H range 3.6 to 7.3. The rate of filtration of tan liquors is markedly affected by change of p_H value, which may be attributed to changing degrees of dispersion of some of the solid matter. The addn. of lime to tan liquors causes a pptn. of tannin, but only at p_H values greater than 7.2.

J. A. WILSON

The biochemical properties of hide substance and leather. GEORG GRASSER. *Z. Leder Gerberei-Chem.* 1, 259-86(1922).—The properties of the skin constituents are described. The effects of various stains on hide during its conversion into leather by various methods of tannage were examined and are noted in tables. (Not suitable for detailed abstract.—ABSTR.)

F. L. SEYMOUR-JONES

The influence of atmospheric humidity on the strength and stretch of leather. F. P. VEITCH, R. W. FREY AND L. R. LEINBACH. *J. Am. Leather Chem. Assoc.* 17, 492-508(1922).—Strips, 10 cm. \times 1 cm., were cut from an area 66 cm. \times 45 cm. from three sides of lightly vegetable tanned calfskin which was not loaded, stuffed, or fat-liquored. These were conditioned in a room of const. humidity at 70° at various relative humidities (R. H.) until equil. They were then broken on a 200 kg. vertical Scott tester at 70°, the strength and stretch being noted. Strips from the three sides were all conditioned at 35 percent R. H.; all from the first and half of those from the second and third were tested at this R. H. The other halves were reconditioned at 55 and 75 percent R. H., respectively, and tested at those R. H. The results for individual pieces in each set varied widely. Averages showed that both strength and stretch were considerably greater as the R. H. increased. The effect on oiled or stuffed leathers would probably be less, but it is important that all tests on tensile strength, to be comparable, should be carried out at a definite R. H.

F. L. SEYMOUR-JONES

Determination of optimum temperature for maximum extraction of tannin from sundri bark. B. B. DHAVAL AND S. R. DAS. *J. Soc. Leather Trades' Chem.* 6, 311-5(1922).—The optimum temp. for the max. extn. of tannin from sundri (*Heritiera minor*) bark was detd. in the same manner as that of goran bark (*C. A.* 16, 4088) and was found to be 65-70°, with a tans/non-tans ratio of 2.156. F. L. SEYMOUR-JONES

Centrifugal force and the colloidal state in tanning extracts. EM. DRPASSE. *Cuir* 1922, 491-6.—Vegetable tannin solns. at 90° consist of a hydrophilic dispersion. On cooling, part of the dispersed material coagulates, part changes to hydrophobic dispersion, while the bulk of the tannin remains hydrophilically dispersed. While the coagulum rapidly settles, the suspensoid (hydrophobic dispersion) only settles slowly. Since the suspensoid is negatively charged, settling may be accelerated by (a) pptn. with a trivalent positive ion, e. g., Al^{+++} ; (b) pptn. with a positively charged colloid, e. g., kaolin, powdered chalk. After removing the suspensoid and coagulum, the emulsoid tannin, which is also negatively charged, must be peptized, as otherwise it is pptd., although more slowly. The centrifuge may be applied to clarifying tanning exts. The material is leached as usual, concd. to a degree suitable for the centrifuge, cooled, centrifuged and then evapd. to the desired consistency.

F. L. SEYMOUR-JONES

Some notes on synthetic tannins (syntans). U. J. THUAU AND A. T. HOUGH. *J. Soc. Leather Trades' Chem.* 6, 308-11(1922).—The authors review the practical uses and advantages of syntans. They assume that vegetable tan liquors are colloidal solns. containing a peptizer and a peptized substance, which latter ppts. on the skin fibers. Syntans also contain these two substances, but, when present together with vegetable

tannins, act predominately as peptizers, rendering the insolubles soluble. It is shown by expt. that the addition of a syntan to a tan liquor decreases the amt. of insolubles.

Progress in tanning in 1921. R. LAUFFMANN. *Gerber* 1922, 59-60, 69, 99-101, 113-4, 120-2, 135-6, 143-5, 152-6, 161-3.—An uncritical summary of individual papers on leather trades' chemistry arranged according to subject. F. L. SEYMOUR-JONES

Chrome tanning. XI. Some observations on the properties of the common chrome liquors. D. BURTON, R. P. WOOD AND A. GLOVER. *J. Soc. Leather Trades' Chem.* 6, 281-7(1922); cf. *C. A.* 16, 3230.—A series of chrome liquors, of identical Cr content and basicity, was prepared by (a) reducing $K_2Cr_2O_7$ with glucose, SO_2 , sawdust, whey, and spent tan; (b) neutralizing Cr alum with NaOH. The behavior on dilution and the amt. of alkali required to bring the liquor to the pptn. point (pptn. figure) were studied. All liquors remained clear and bright on dilution except the whey, which gave slight ppts. on standing overnight. The pptn. figure was detd. by adding 0.1 N NaOH at a const. rate and temp. to 10 cc. of the liquor until a faint turbidity appeared. This figure varies with the age of the liquor, increasing with age for the SO_2 and Cr alum liquors and decreasing for the others. At equil. the pptn. figures are in the order: glucose, SO_2 , > sawdust, spent tan, whey, > Cr alum. Postulating a negatively charged Cr complex as the tanning agent, it will increase in amt. with decreasing hydron concn. and *vice versa*.

F. L. SEYMOUR-JONES

The chroming of formaldehyde leather. E. GRILICHES. *Collegium* 1922, 199-201.—The amt. of Cr taken up by hide was found to be not appreciably altered when pieces of horse hide grain splits were given a pre-tannage in HCHO. When normal solns. of $Cr_2(SO_4)_3$ were used in place of the usual basic ones, the pre-tannage with HCHO caused greater Cr fixation. The pre-tanned leather takes up less acid from the liquor than the straight chrome-tanned leather.

F. L. SEYMOUR-JONES

The behavior of synthetic tannins containing sulfo groups in tanning chemistry. W. MOELLER. *Z. Leder Gerberet-Chem.* 1, 303-8(1922); cf. *C. A.* 16, 2792.—Certain synthetic tannins readily hydrolyze hide while others do not. This latter effect may be due to compensation of the sulfo group by an amino group in the tannin molecule. Dil. solns. of sulfanilic, aminonaphtholsulfonic, and naphthylaminosulfonic acids were allowed to act on hide powder for periods of 1, 2, and 3 weeks. The hydrolyzed polypeptides and peptones were pptd. with phosphotungstic acid and the N in soln. was estd. before and after pptn. No appreciable hydrolysis was found. F. L. S.-J.

Manufacture of ready-made stable fat-liquor from Indian oils. I. B. M. DAS AND S. R. DAS. *J. Soc. Leather Trades' Chem.* 6, 328-35(1922).—Madras sardine oil was sulfonated, washed, extd. with brine, and neutralized with ammonia, yielding a yellowish, creamy fat. This was rendered liquid by treatment with petroleum. To give the fat-liquor stability and body, a soft potash-castor-oil soap was added together with another oil. Only castor and spindle oils proved suitable for this purpose. The fishy smell of the sardine oil largely disappeared on sulfonation and was not apparent in the finished leather. A local com. castor oil was similarly sulfonated, washed, extd. with brine, and neutralized with NaOH. To this Turkey-red oil liquid soap, spindle and castor oils were added, the best proportions being, by wt., 4 : 3 : 1 : 1, resp.

F. L. SEYMOUR-JONES

Unhairing hides. G. DUCKWORTH. *Brit.* 186,608, Sept. 19, 1922. Skins are treated for the removal and recovery of the fur and hair without impairing the usefulness of the skins for the production of leather, by immersing them in a 3% soln. of Na_2SO_4 for 12 hrs., then in a soln. of NH_4OH for 12 hrs. at 80-120° and finally subjecting them to a sweating process for 12-24 hrs. The soln. of NH_4OH contains about 4 pt. of 0.880

NH_3 in 4 gal. of H_2O . The hair should be removed by scraping or brushing as soon as possible after the removal of the skins from the sweating vat.

Treating skins, etc. C. P. BOSSERT. Brit. 186,482, Aug. 3, 1921. In a machine for applying a thick plastic substance to an article, particularly for applying a hair-removing compd. such as the sulfides of soda and lime to hides and skins, the substance is applied by an agitating device to a feed-roll from which it is removed and thrown on to the hide or the like supported on a conveyer. A suitable construction is specified.

